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Energy and Environmental Technology

Calcination applying H_2 combustion in O_2 in a CO_2 rich atmosphere

Dipendra Khadka

Faculty of Technology, Natural sciences and Maritime Sciences
Campus Porsgrunn

University of
South-Eastern Norway

www.usn.no

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Student:	Dipendra Khadka
Supervisor:	Prof. Lars André Tokheim
External Partners:	Norcem AS Brevik (Tor Gautestad)
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Summary:

The cement industry is one of the leading producers of anthropogenic greenhouse gases, the most important of which is CO_2. Strong mitigation measures must be introduced to reduce substantial CO_2 emissions from the cement industries. And one of many options to reduce CO_2 emission is to keep direct combustion in the calciner to decarbonize raw meal used in the industry to produce cement clinker by combusting hydrogen fuel rather than carbon containing fuels which will not only eliminate CO_2 formation as a result of fuel combustion but also provide a basis for simple capture of CO_2 produced by calcination, as CO_2 is the only gas that exits from calciner. For this purpose, this thesis research that deals with the calcination of raw meal using H_2 combustion in O_2 in a CO_2 rich atmosphere was carried out.

To study the major impacts in a regular cement kiln process due to the substitution of carbon containing fuel by hydrogen and oxygen fuel, literature study was carried out on a various topics including water electrolysis technologies, safety aspects related to production, handling and storage of hydrogen and oxygen fuel in a cement kiln environment, terminal settling velocity of the raw meal particles and adiabatic flame temperature. A mass and energy balance for steady-state conditions was performed using MATLAB to measure relevant temperature, flow rates, and duties in our modified cement calciner system and heat exchanger. The design basis values were chosen identical to that of Norcem, Brevik.

The major parameters, including terminal settling velocity based on the maximum particle size i.e. 1000 µm (design basis value) and the gas velocity in the calciner were determined to ensure that the raw meal particles are completely entrained from our modified cement calciner system.

The calculation of the adiabatic flame temperature as a result of specific fuel i.e. coal/air combustion implied to calcine the raw meal in Norcem and the adiabatic flame temperature as a result of H_2 combustion in O_2 in a CO_2 rich atmosphere was done using spyder (Python). The main purpose of this calculation was to maintain the substituted fuel's adiabatic flame temperature in our specified system same as the regular coal/air fuel for combustion by adjusting the recycle ratio of CO_2 recycling back to the calciner. As a result of Python plot, recycling of 1.538 moles of CO_2 back to the calciner for every one mole hydrogen and half mole of oxygen fuel combustion was found to be appropriate to maintain the identical flame temperatures.

The other primary goal of this thesis research was to determine the extent to which constructional changes were required for the existing calciner. Two options were concluded based on the results of our design calculation to ensure that the raw meal particles are fully entrained from our new calciner system. The first option is to decrease the diameter of the calciner in comparison to the existing calciner, which raises the CAPEX value while adjusting the recycle ratio of CO_2 to its lower limit i.e. 0.1 resulting in lower OPEX value for our new system. The second option is to ensure that the maximum size of raw meal limestone particles entering the calciner is less than or equal to 500 µm and to adjust the CO_2 recycle ratio to a corresponding value of 0.6, taking into account the current existing calciner with no constructional changes. The total amount of hydrogen and oxygen fuel required were calculated based on the appropriate recycle ratio, and the required capacity and the number of water electrolysis cells needed for our specified system were determined. NEL ASA's commercially available atmospheric alkaline water electrolyzer was choosen for our system.

The cost of the water electrolyzer and CO_2 fan as per required capacity was estimated. Centrifugal radial fan for the purpose to recycle the required amount of CO_2 back to calciner was considered for this project. The annual equivalent capital and operational costs were estimated considering both the appropriate design options mentioned above. Finally, the cost per mass of CO_2 avoided were calculated.

Preface

This master's thesis report, titled "Calcination applying H_2 combustion in O_2 in a CO_2 rich atmosphere," aims to demonstrate not only my own diligence and commitment, but also that of my supervisor, Prof. Lars André Tokheim, in order to meet the graduation criteria for a Master of Science degree in Energy and Environmental Technology.

This master's thesis was created as a part of a research project titled "Combined calcination and CO_2 capture in cement clinker production by use of CO_2-neutral electrical energy" in collaboration between USN and Norcem AS Brevik.

The image on the first page was taken from the website of Norcem, Brevik [1].

Firstly, I'd like to express my heartfelt gratitude and appreciation to Prof. Lars André Tokheim for his invaluable assistance during the project. I'd also like to thank Mr. Christoffer Moen, a laboratory manager at Norcem Brevik for his time and support. Last but not least, I would like to thank my family for their unwavering support throughout these two years of completing the master's degree.

Porsgrunn, 19.05.2021

Dipendra Khadka

Contents

Nomenclature

List of symbols

Symbol	Description	Unit
A_{cal}	Cross-sectional area of the calciner	[m^2]
Ar	Archimedes number	[-]
$A_{p,proj}$	Projected area of the particle	[m^2]
a_f	Annuity factor	[-]
C_D	Drag coefficient	[-]
$C_{p,PM}$	Specific heat at the constant pressure of preheated meal at T_{PM}	[J/kg·K]
C_{p,H_2}	Specific heat at the constant pressure of hydrogen fuel at T_{H_2}	[J/kg·K]
C_{p,O_2}	Specific heat at the constant pressure of oxygen fuel at T_{O_2}	[J/kg·K]
$C_{p,CO_2,r}$	Specific heat at the constant pressure of CO_2 recycling back to calciner at $T_{CO_2,r}$	[J/kg·K]
$C_{p,CO_2,c}$	Specific heat at the constant pressure of CO_2 at T_c	[J/kg·K]
$C_{p,meal,c}$	Specific heat at the constant pressure of calcined meal at T_c	[J/kg·K]
$C_{p,H_2O,c}$	Specific heat at the constant pressure of water vapor at T_c	[J/kg·K]
$C_{p,CO_2,HEX}$	Specific heat at the constant pressure of CO_2 at the average temperature of the hot side	[J/kg·K]
$C_{p,H_2O,HEX}$	Specific heat at the constant pressure of H_2O at the average temperature of the hot side	[J/kg·K]
$C_{p,air,HEX}$	Specific heat at the constant pressure of air at the average temperature of the cold side	[J/kg·K]
$C_{el,kWh}$	Cost of electricity per kWh	[NOK/kWh]

$\mathrm{C_{el,yr}}$	Cost of equivalent electricity per year	[MNOK/y]
$\mathrm{C_{2002}}$	Cost-index value in 2002	[$]
$\mathrm{C_{2011}}$	Cost-index value in 2011	[$]
$\mathrm{C_{2021}}$	Cost-index value in 2021	[$]
D_{cal}	Diameter of the calciner	[m]
D_p	Diameter of the particle	[µm]
$d_{p,max}$	Maximum size of raw meal particle	[µm]
$\varepsilon_{el,we}$	Total electrical power required for water electrolyzer	[MW]
ε_c	Power consumption by water electrolzer	[kWh/Nm^3]
E_{PM}	Energy in a preheated meal	[J/s]
$E_{gen,c}$	Generated energy	[J/s]
$E_{in,c}$	Inlet energy	[J/s]
$E_{out,c}$	Outlet energy	[J/s]
e	Elementary charge	C
f	Actual fuel-air ratio	[-]
f_s	Stoichiometric fuel-air ratio	[-]
$f_{TIC,CS}$	Total installed cost factor of CS material	[-]
$f_{EQ,CS}$	Cost factor for CS equipment from DFT	[-]
$f_{PI,CS}$	Cost factor for CS piping from DFT	[-]
F	Faraday’s constant	[-]
F_D	Drag force	[Newton]
H_c	Enthalpy of calcination	[MJ/kg$_{\mathrm{CO2}}$]
H_{calc}	Height of calciner	[m]

H_r	Enthalpy of reactant	[J]
H_p	Enthalpy of product	[J]
h_{si}	Sensible enthalpy	[kJ/mol]
I	Current withdrawn by each cell	[Coulomb/s]
M_{CaCO_3}	Molecular mass of $CaCO_3$	[kg/mol]
M_{CO_2}	Molecular mass of CO_2	[kg/mol]
M_{H_2}	Molar mass of hydrogen	[kg/mol]
M_{H_2O}	Molar mass of water vapor	[kg/mol]
M_{o_2}	Molar mass of oxygen	[kg/mol]
$\dot{m}_{CMR}$	Mass flow rate of calcined meal	[t/h]
$\dot{m}_{CO_2,m}$	Total CO_2 generated by meal in pre-calciner	[t/h]
$\dot{m}_{CO_2,r}$	Mass flow rate of recycle CO_2	[t/h]
m_f	Material factor	[-]
$\dot{m}_{H_2}$	Required amount of hydrogen fuel for our specified system	[t/h]
$\dot{m}_{PM}$	Mass flow rate of preheated meal	[t/h]
$\dot{m}_{H_2,A3880}$	Water electrolyzer hydrogen production rate	[kg/day]
N_A	Avogadro’s number	[-]
N_{ec}	Number of water electrolysis cell	[-]
N_{fuel}	Number of moles of fuel	[mol]
$N_{i,P}$	Number of moles of product species	[mol]
$N_{i,R}$	Number of moles of reactant species	[mol]
n_{o_2}	Number of moles of oxygen from our combustion settling	[mol]

$\dot{n}_{CO_2,r}$	Molar flow rate of recycle CO_2	[mol/h]
n_{w-el}	Efficiency of water electrolyzer	[%]
P	Pressure	[atm]
$\dot{P}_{H_2}$	Net production rate of hydrogen	[Nm^3/h]
Q^o_{rxn}	Heat of reaction	[kJ/mol]
R	Universal gas constant	$\left[\frac{\mathrm{atm} \cdot \mathrm{L}}{\mathrm{gmol} \cdot \mathrm{K}}\right]$
Re	Reynold’s number	[-]
r_r	Recycle ratio of CO_2	[-]
$\mathrm{r}_{\mathrm{CI,f}}$	Cost-index ratio	[-]
T_P	Temperature of product	[K]
T_c	Calcination temperature	[K]
$T_{air,in}$	Inlet temperature of air from clinker cooler	[K]
$T_{CO_2,r}$	Temperature of CO_2 recycling back to the calciner	[K]
$T_{(CO_2+H_2O),in}$	Inlet temperature of gas streams exiting from calciner	[K]
$T_{(CO_2\&H_2O),ex}$	Exit temperature of gases exiting from heat exchanger	[K]
$T_{air,exit}$	Exit temperature of heated air stream	[K]
T_{H_2}	Temperature of hydrogen fuel entering the calciner	[K]
T_{O_2}	Temperature of oxgyen fuel entering the calciner	[K]
T_R	Temperature of reactant	[K]
T_{ref}	Reference temperature	[K]
T_{PM}	Temperature of preheated meal	[K]
$t_{gas,r}$	Gas residence time	[s]

V_t	Terminal settling velocity	[m/s]
V_{gas}	Velocity of gases in the calciner	[m/s]
$\dot{V}_{gas}$	Volumetric flow rate of gas in the calciner	[m^3/s]
$\Delta h°$	Enthalpy of formation	[kJ/mol]
$\emptyset$	Equivalence ratio	[-]
ρ_{gas}	Density of fluid	[kg/m^3]
μ	Dynamic viscosity of fluid	[Pa.s]

List of Abbreviations

AEC	Alkaline Electrolysis Cell
AFT	Adiabatic Flame Temperature
CAPEX	Capital Expenditure
CS	Carbon Steel
DFT	Detailed Factor Table
EAC	Equivalent Annual Cost
HHV	Higher Heating Value
LHV	Lower Heating Value
NPV	Net Present Value
OPEX	Operational Expenditure
PHM	Pre-Heated Meal
SOEC	Solid Oxide Electrolysis Cell
TIC	Total Installed Cost

1 Introduction

This chapter includes background, objectives of the study and organization of the report.

1.1 Background

One of the leading producers of the anthropogenic greenhouse gases, of which CO_2 is most significant, is the cement industry. The industry emits around 900kg of CO_2 with every 1000kg of cement produced. An average of more than 3.5 billion tons of cement are produced annually. This estimation equates over 3 billion tons of CO_2 produced per year [2]. Cement plants not only emit CO_2, but also Sulphur dioxide (SO_2), and nitrous oxides (NO_X) contributing to greenhouse effect and acid rain. However, the following master's thesis study deals particularly with CO_2 only.

There are two major aspects of cement production that results in the emission of CO_2. First is calcination, which is a strong endothermic reaction occurring at approximately 900°C responsible for thermal decomposition of limestone ($CaCO_3$) into lime (CaO) and carbon dioxide (CO_2). This process accounts for about 65% of CO_2 emission. Additionally, 35% comes from combustion process [3].

1.2 Problem description

To reduce significant emission of CO_2 from cement industries, strong mitigation strategies needs to be implemented. And one out of many alternative to reduce CO_2 emission is to keep direct combustion in the calciner to decarbonate raw meal by combusting hydrogen rather than carbon containing fuels which will not only eliminate CO_2 formation as a result of fuel combustion but also provide a basis for simple capture of CO_2 generated by calcination since CO_2 is the only gas that exits from calciner [3].

Hydrogen will play an important role as a potential energy carrier (and carbon-free fuel) for sustainable development in the future. Biomass processing, biological and solar thermal water splitting, or water electrolysis are some of the methods that offer renewable and clean hydrogen fuel production [4]. Water electrolysis is a promising option for green hydrogen production from renewable sources. The environmental feasibility, technical and economical sustainability of the use of hydrogen generated via water electrolysis for the purpose of combustion fuel to calcine the raw meal in calciner will generally be studied in this current master's thesis.

1.3 Objectives of the study

The main objective of this master's thesis project is to research the major impacts of the substitution of carbon containing fuel used in cement industry to calcine the raw meal with hydrogen and oxygen fuel for combustion and decarbonization of raw meal in calciner.

In order to achieve the objective of the project, project goals are categorized as follow:

1. Evaluating different types of water electrolyzer along with their potential energy losses.
2. Investigating the flame properties as a result of H_2 combustion in O_2 in a CO_2 rich atmosphere.
3. Making a flow diagram for the required simulation case.
4. Calculating temperatures, flow rates and duties with application of mass and energy balance equations.

5. Making a process simulation model and simulate various cases, varying key system parameters.
6. Determining the required size of the different project equipment's that includes electrolyzer, calciner, condenser, gas ducts, and the CO_2 fan.
7. Estimating investment costs (CAPEX) and operational costs (OPEX) of the process per avoided CO_2 unit (€/tco_2)

To fulfill the project's requirements and goals, it is important to address some main questions:

1. What are the different water electrolysis technologies to produce H_2 & O_2 gas and potential energy losses during the process?
2. How the replacement of the fuel for calcination be more feasible than the current method?
3. What are the safety aspects related to production, handling and combustion of hydrogen and oxygen in a cement kiln environment?
4. What are the temperatures, duties and flow rate values in the new system?
5. How much CO_2 must be recycled?
6. To what extent constructional changes to the existing calciner system are required?
7. What are the major impacts on cement kiln process?
8. What is the estimated cost of the new system?

The task description and Work Breakdown Structure are presented in Appendix A and B respectively.

1.4 Organization of the report

The report is organized into seven major chapters. The first chapter begins with an introduction that includes background information, a description of the problem, and the thesis objectives. The second chapter includes a review of the literature as well as theory related to the scope of the thesis. It includes process description of the regular and modified cement kiln system, water electrolysis technologies, and other key theories including adiabatic flame temperature, terminal settling velocity and safety aspects related to the production, handling and storage of hydrogen and oxygen in a cement kiln environment. Mass and energy balance methods and calculations followed by terminal settling velocity, gas velocity in the calciner and AFT calculations are presented in third chapter. All procedures and design calculations for the relevant equipment units required for the specified system of this project are included along with discussion in chapter 4. Cost estimation theory and estimated cost of the new system are presented and discussed in fifth and sixth chapter, respectively. Lastly, the conclusion is summarized in the seventh chapter.

2 Theory and literature review

This section begins with a general overview of regular and modified cement kiln system followed by different types of water electrolysis technologies and the discussion of various theories required for the design of equipment units involved with the project.

2.1 Process description

2.1.1 The regular cement kiln system

The regular cement kiln system composes of preheater towers consisting of series of vertical cyclone, calciner also known to be pre-calciner, rotary kiln also known to be post-calciner and clinker cooler as shown in below Figure 2.1. The raw meal enters at the top of preheaters and is heated to approximately 700° C by hot gases from the calciner. Most of the preheated meal is calcined at 900° C in the calciner by the additional heat liberated by the energy of fuel combustion resulting in decarbonation of limestone based raw materials with a calcination degree of about 94%. During the decarbonation of raw meal, CO_2 is produced($CaCO_3 \rightarrow CaO + CO_2$). Thus, CO_2 is formed during two stages: one during the combustion of fuel and other during decarbonation. After then, the pre-calcined meal is first fully calcined in the rotary kiln before being heated further until cement clinkers are formed at the temperature ranging from 1400°C–1450°C. Finally, in the clinker cooler, clinker is cooled by ambient air. A significant portion of heated air in the cooler is used as secondary air in the rotary kiln and tertiary air in the calciner [3]. However, some low temperature heat around 200°C is lost to the surroundings.

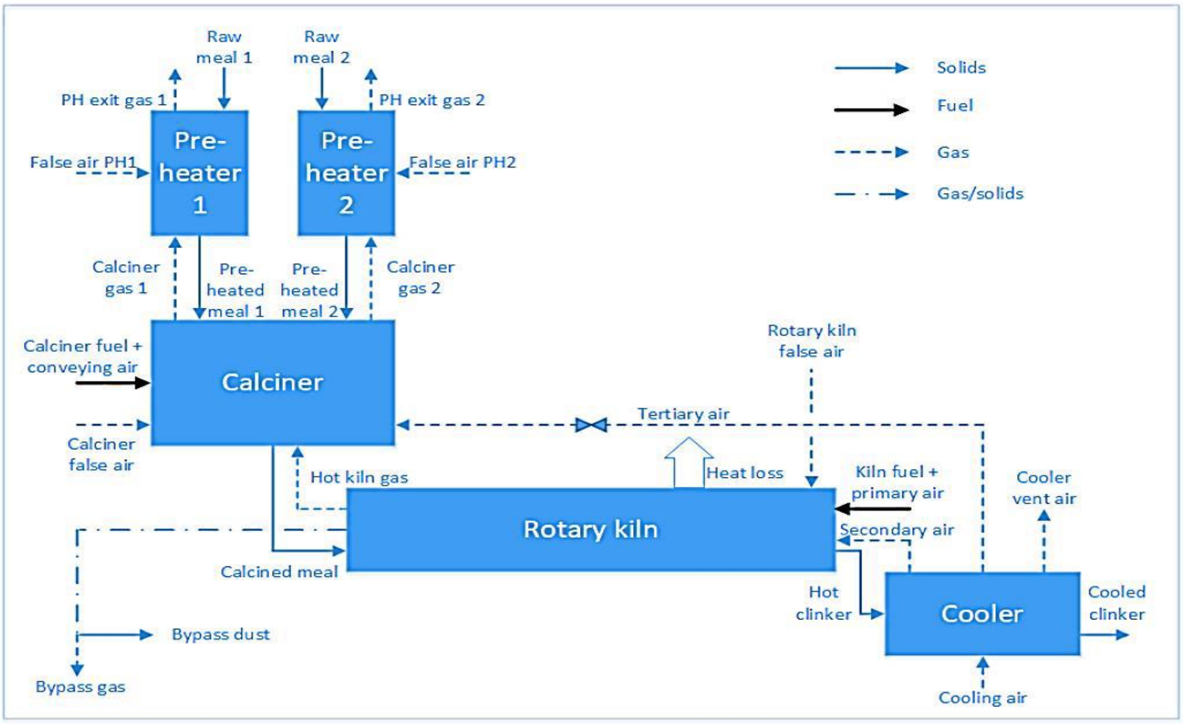


Figure 2.1: A regular cement kiln system with two preheaters [3]

2.1.2 Modified cement kiln system applying hydrogen combustion

In a Figure 2.2 below, a hypothetical implementation of calciner system is depicted, suggesting hydrogen combustion in oxygen in a carbon dioxide rich atmosphere to pre-calcine the raw meal. A carbon containing fuel that is used to calcine the meal in a regular cement kiln system is replaced by hydrogen fuel. The key idea behind this design is to keep direct combustion in a calciner and prevent CO_2 formation by combusting hydrogen instead of any other carbon containing fuels. This also has the significant benefit of ensuring direct heat transfer between combustion products and the meal while obviating the need for additional heat transfer surfaces [3].

In a process, electrical energy is used to dissociate liquid water into hydrogen and oxygen gas by the means of water electrolyzer. The mixture of hydrogen and oxygen gas is mixed with recycled carbon dioxide gas for the purpose to control temperature in the process and also to prevent explosions [3]. In the calciner, this mixture is then combusted. Hot CO_2 along with some water vapor exiting from calciner pass through heat exchanger in order to utilize the heat from hot gases back to pre-heater tower. A cooled CO_2 and H_2O exiting from heat exchanger passes through condenser where pure CO_2 gas is separated from liquid water. Some portion of CO_2 gas is recycled back to the calciner.

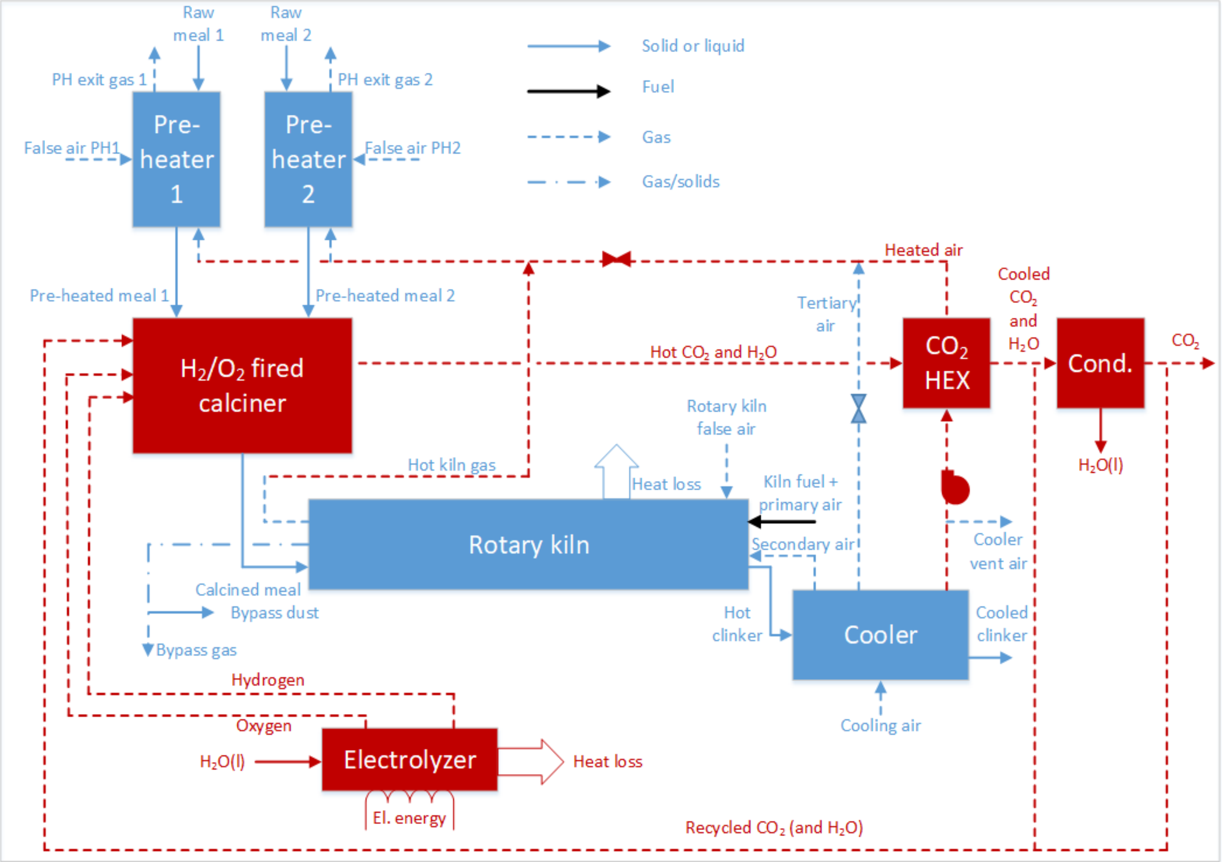


Figure 2.1: The modified cement kiln system applying hydrogen combustion for calcination

2.2 Introduction to water electrolysis

The advancement of green hydrogen production technologies in order to substitute fossil fuel-based hydrogen production methods is a critical move toward creating a long-term hydrogen economy [5]. The method of decomposing water into hydrogen and oxygen gas by the means of electricity is called water electrolysis. This process is the cleanest way of producing hydrogen when the necessary electricity is provided by renewable sources of energy. Approximately 5% of global hydrogen gas produced is generated by electrolysis [6]. The overall process of water division as a result of electrolysis is as follows:

$$H_2O \xrightarrow{2F} H_2(g) + \frac{1}{2}O_2(g)$$

$F=N_A \cdot e$ represents Faraday's constant denoting 1 mol of electric charge. where,

N_A= Avogadro's number = 6.022×10^{23} and "e" is the elementary charge equals to 1.602×10^{-19} C.

Regardless of the form of electrolysis, the main component of the water electrolysis unit consists of an anode, an electrolyte-separated cathode, and a power supply. The current majority of research and development for renewable hydrogen production have focused on three major water electrolysis technologies which will be further discussed as a part of this research project and they includes: Alkaline Electrolysis Cells (AEC), Proton Exchange Membrane Electrolysis Cells (PEMEC) and Solid Oxide Electrolysis Cells (SOEC) [7].

2.2.1 Alkaline water electrolysis

AEC is one of the mature water electrolysis technology and is generally used for large scale industrial applications. The general characteristics of the AEC are pictured in Figure 2.3. Two electrodes are immersed in an alkaline solution (typically at a concentration of approx. 40% aqueous KOH or NaOH solution) [8]. During the process only water is consumed, and water must therefore be supplied to the cell to feed the reaction and maintain the electrolyte concentration at the optimal value. Oxygen and Hydrogen are separated from the water when the direct current is applied to the electrodes according to the following half-cell reactions:

At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Typically, the electrodes are separated by microporous separator (with a thickness between 0.050 to 0.5 mm) basically known as diaphragm. The most common type of diaphragm in AEC is asbestos ($Mg_3Si_2O_5(OH)_4$) and used for the purpose to segregate hydrogen and oxygen gases [9]. However, several researches are being conducted for the development of advanced diaphragm since the corrosion rate of typical diaphragm used recently i.e. asbestos tends to be corrosive while operated at high temperature in an attempt to increase efficiency of the respective electrolyzer. AEC systems have a relatively low capital cost due to the avoidance of noble metals as catalyst but due to its limited dynamic operation, low current density and operating pressure, the hydrogen production cost, efficiency, and gas purity are negatively impacted. Usually, operating current densities are limited to the range of 400-500mA/cm^2 and the specific energy consumption in order to produce hydrogen gas ranges from 4.1 to 4.5

kWh/Nm^3 H_2 at 0.45 A/cm^2. The hydrogen production efficiency is approximately 80% with a purity of about 99% [10].

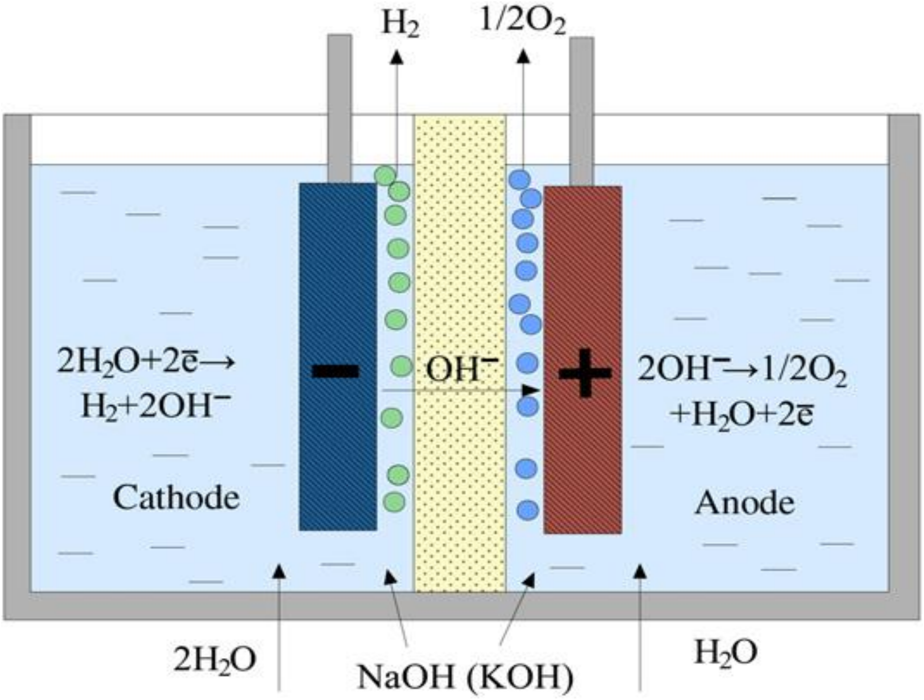


Figure 2.2: Schematic diagram of Alkaline Electrolysis Cell [10]

2.2.2 Solid oxide water electrolysis

The basic characteristic features of SOEC technology is shown in Figure 2.4. As an electrolyte and cell separator, SOECs uses solid ion conducting ceramics that allows system to operate at relatively higher temperatures usually at the range of (800-1000) °C. The splitting of water steam is followed by following half cell reactions where water molecules are reduced at cathode and the resulting oxygen shift to anode, where oxygen is formed as follows:

At Cathode: $H_2O_{(g)} + 2e^- \rightarrow H_{2(g)} + O^{2-}$

At anode: $2O^{2-} - 2e^- \rightarrow O_{2(g)}$

This technology of electrolysis is not widely commercialized and have been only developed and tested in a laboratory scale [11]. A cell voltage of usually 1.2-1.3 V is used which corresponds to an electricity consumption of 2.8-3.0 kWh/Nm^3 H_2. High electrical performance and low capital cost are some of the SOECs possible benefits. The issue with design of system for high temperatures and structural materials, however, has not yet been fully resolved [10].

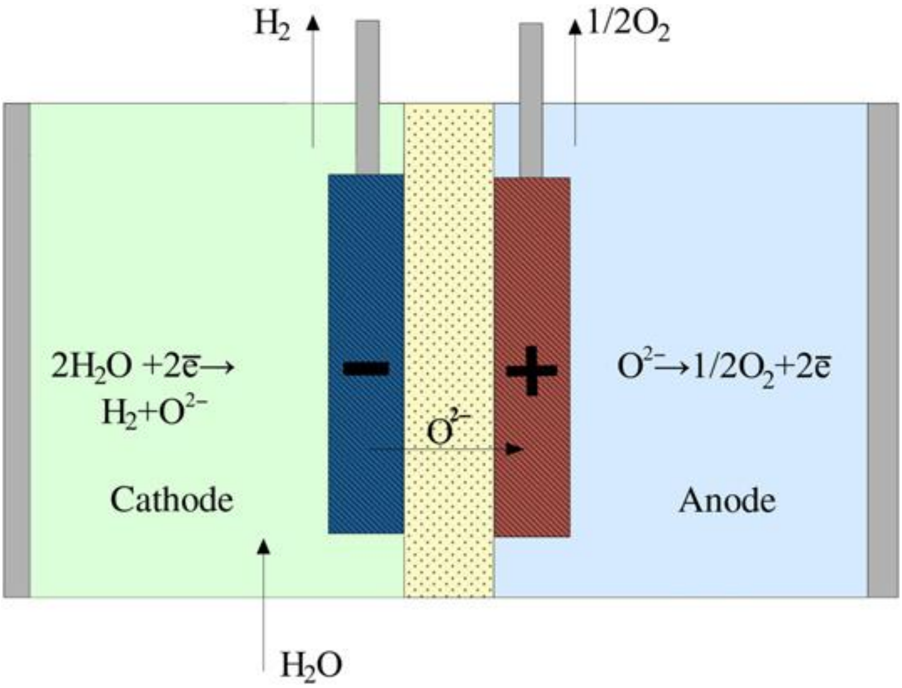


Figure 2.2: Schematic diagram of Solid Oxide Water Electrolysis [10]

2.2.3 Proton exchange membrane water electrolysis

PEMEC is the water electrolysis system based on solid polymer electrolyte(SPE) and are considered to be most effective technology to produce hydrogen from water [12]. This technology was first introduced by Generic electric in the late 1960s to overcome the cons of AECs including low current density and low-pressure operation. PEM electrolyzers have many advantages over conventional alkaline electrolysis systems, including environmental cleanliness, ease of maintenance, compactness, and so on [13]. Comparison of AECs and PEMECs water electrolysis technology is presented in Table 2.1 [10]. The general working principle of PEMEC is presented in Figure 2.5. SPE materials made up of perfluorosulfonic acid is used to operate respective fuel cells which has a relatively high mechanical strength and proper chemical stability. Two electrodes are pressed against SPE resulting in the formation of so-called Membrane Electrode Assembly (MEA). Hydrogen ions migrate across the SPE and hydrogen gas is formed at cathode while oxygen formation takes place at anode as a following half cell reactions:

$$\text{At cathode: } H^{+} + 2e^{-} \rightarrow H_2$$

$$\text{At anode: } H_2O \rightarrow \frac{1}{2}O_2 + 2e^{-} + 2H^{+}$$

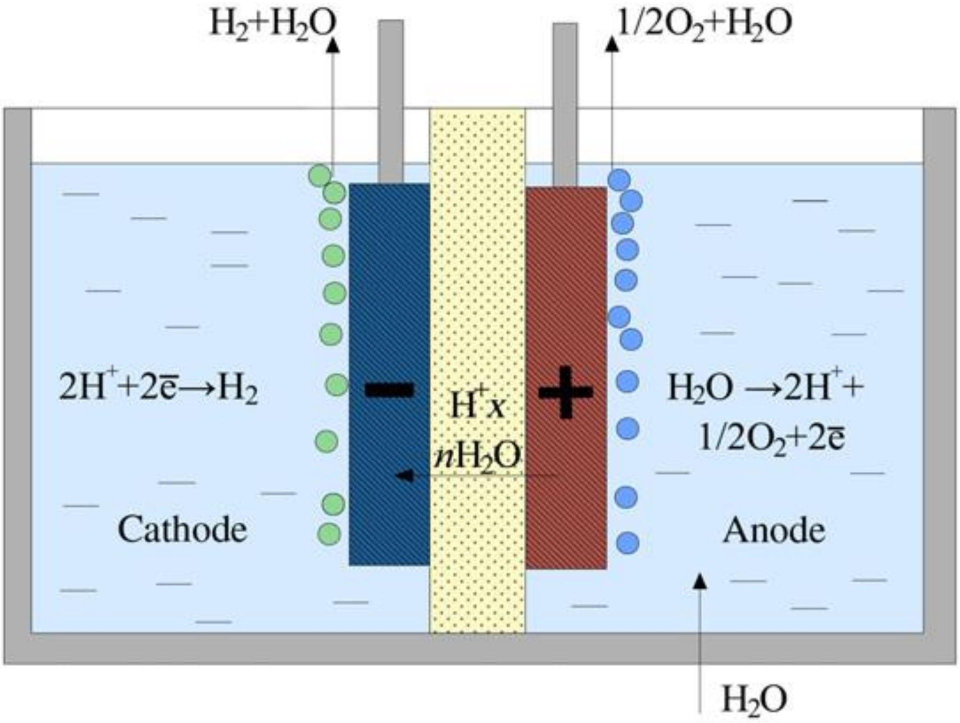


Figure 2.2: Schematic diagram of PEM water electrolysis [10]

When it comes to the efficiency of the electrolysis system, the effect of some key parameters such as operating temperature, electrolyte membrane thickness, current density, heat exchanger effectiveness, and H_2O inlet flow rate are critical [14]. Reversible voltage that causes breakdown of the circuit and minimizing the water electrolyzer efficiency results from overpotential losses that depends on the parameters mentioned below in Table 2.1.

Table 2.1: Comparison of Alkaline and PEM water electrolysis technologies [10]

Parameters	Alkaline Water Electrolysis	PEM Water Electrolysis
Electrolyte	Caustic solution	Polymer electrolyte
Nominal current density	0.45 A/cm^2	1.0 A/cm^2
Energy consumption	4.35 kWh/Nm^3 at 0.45 A/cm^2	4.35 kWh/Nm^3 at 1.0 A/cm^2
Maximum current density	0.8 A/cm^2	1.0 A/cm^2
H_2 delivery pressure	Up to 30 bar	Up to 700 bar
H_2 purity (dry basis)	≥ 99.9%	≥ 99.99%

Lifetime	≥ 60,000 h	≥25,000 h

2.3 Adiabatic flame temperature

AFT that stands for Adiabatic Flame Temperature is a maximum temperature that can be achieved when all the heat liberated by the combustion reaction goes into heating the product, with no heat transfer at the boundary. Determination of adiabatic flame temperature is very important for the people working in a field that deals with combustion and explosions and also to maximize starting ratio of their reactions for the purpose of maintaining ideal combustion result [15].

Figure 2.6 below depicts the graphical explanation of determining adiabatic flame temperature. The enthalpy of the product mixture is lower than that of reactant mixture at the initial reactant temperature. The energy released during combustion is used to heat up the products such that the condition $H_P(T_P) = H_R(T)_R$ is met under adiabatic constant pressure process analysis [16].

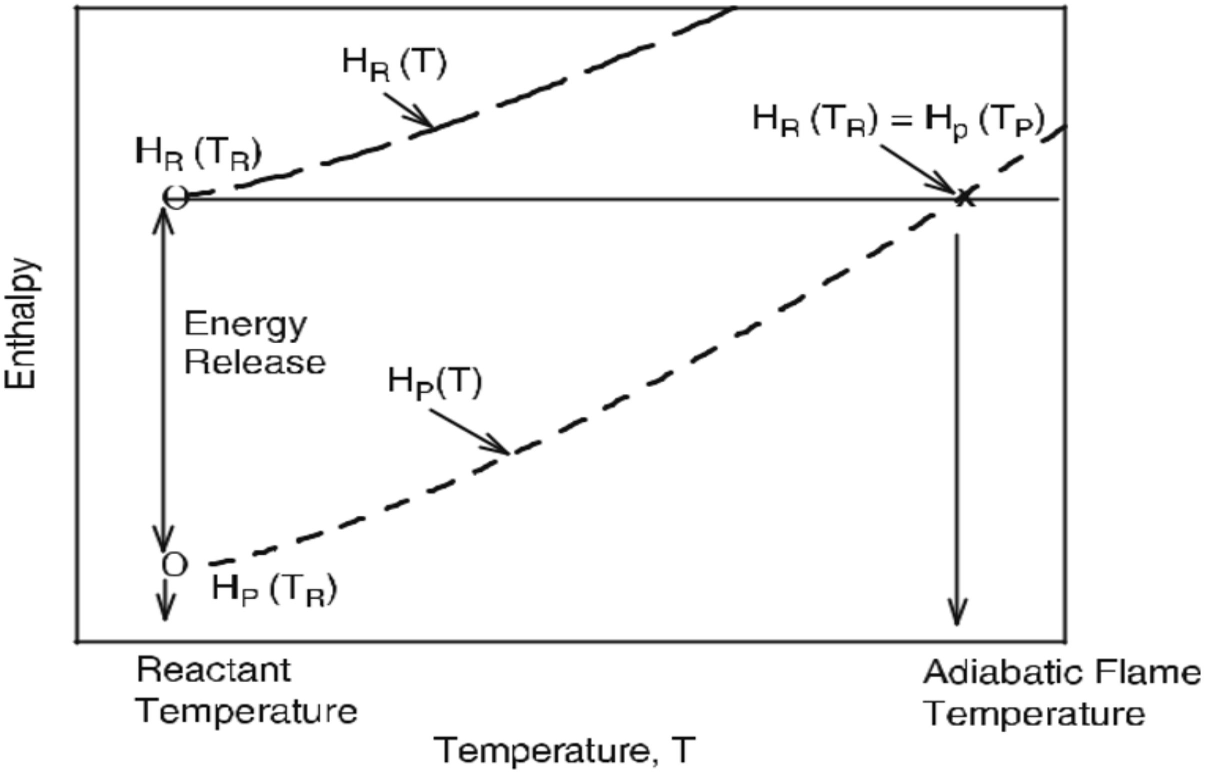


Figure 2.3: Graphical interpretation of adiabatic flame temperature [16]

2.3.1 Methods of determining adiabatic flame temperature

To determine the final temperature of combustion product, three methods can be used which are listed below: -

2.3.1.1 Method I: Constant, average specific heat method

According to the conservation of energy,

$$H_P(T_P) = H_R(T_R) \tag{2.1}$$

which can be expressed as

$$\Sigma N_{i,P}[\Delta h^o_{i,P} + h_{si,P}(T_P)] = \Sigma N_{i,R}[\Delta h^o_{i,R} + h_{si,R}(T_R)] \tag{2.2}$$

where, “i” represents number of species, $N_{i,P}$ & $N_{i,R}$ are the number of moles of reactant and product species, T_P and T_R are the temperatures of reactant and product, Δh° is the enthalpy of formation and h_{si} is the sensible enthalpy.

Rearranging equation 2.1, we get

$$\Sigma N_{i,P} h_{si,P}(T_P) = -\left[\Sigma N_{i,P}\Delta h^o_{i,P} - \Sigma N_{i,R}\Delta h^o_{i,R}\right] + \Sigma N_{i,R} h_{si,R}(T_R) \tag{2.3}$$

$$= -Q^o_{rxn,P} + \Sigma N_{i,R} h_{si,R}(T_R) \tag{2.4}$$

Heat of reaction(Q^o_{rxn}) is the change in enthalpy of a chemical reaction or also defined as the difference between the enthalpies of product species to the enthalpies of reactant species. i.e.

$$Q^o_{rxn,P} = \Sigma N_{i,P}\Delta h^o_{i,P} - \Sigma N_{i,R}\Delta h^o_{i,R} \tag{2.5}$$

To determine sensible enthalpy of product species, assuming that the sensible enthalpy can be approximated by $h_{si,P}(T_P) \approx c_{pi}\,(T_p - T_r)$ with $c_{Pi} \approx constant$, we have

$$(T_P - T_R)\Sigma N_{i,P}c_{Pi} = -Q^o_{rxn,P} + \Sigma N_{i,R}h_{si,R}(T_R) \tag{2.6}$$

Rearranging above equation 2.3, we get

$$T_p = T_r + \frac{-Q^o_{rxn,P} + \Sigma N_{i,R}h_{si,R}(T_R)}{\Sigma N_{i,P}c_{Pi}} \tag{2.7}$$

Sensible enthalpy of any species at standard reference temperature i.e. 25°C is zero [17]. Thus, equation becomes

$$T_p = T_r + \frac{-Q^o_{rxn,P}}{\Sigma N_{i,P}c_{Pi}} \tag{2.8}$$

Since due to high combustion temperature, water in the product is likely in gas phase. Thus, $-Q^o_{rxn,p}$ = LHV · N_{fuel} · M_{fuel}, where N_{fuel} & M_{fuel} are the number of moles and molecular weight of fuel. Hence, adiabatic flame temperature using constant average specific heat method can be approximated as:

$$T_p = T_r + \frac{\mathrm{LHV}.N_{fuel}M_{fuel}}{\Sigma N_{i,P}c_{Pi}} \tag{2.9}$$

2.3.1.2 Method II: Iterative enthalpy balance method

Finding the flame temperature by iteratively assigning the flame temperature (T_p) until $H_P(T_P) \approx H_R(T_R)$ is a more accurate approach. The enthalpy of product and reactant can be expressed as follows:

$$H_P(T_P) = \Sigma N_{i,P} h_{i,P} = \Sigma N_{i,P}[\Delta h^o_{i,P} + h_{si,P}(T_P)] = H_R(T_R) = \Sigma N_{i,R} h_{i,R} \qquad (2.10)$$

To determine the expression of sensible enthalpy, rearranging equation 2.7, we get

$$\begin{aligned} \Sigma N_{i,P}\Delta h^o_{i,P} + \Sigma N_{i,P} h_{si,P}(T_P) &= \Sigma N_{i,R}\Delta h^o_{i,R} + \Sigma N_{i,R} h_{si,R}(T_R) \\ \Sigma N_{i,P} h_{si,P}(T_P) &= \Sigma N_{i,R}\Delta h^o_{i,R} - \Sigma N_{i,P}\Delta h^o_{i,P} + \Sigma N_{i,R} h_{si,R}(T_R) \qquad (2.11) \\ \Sigma N_{i,P} h_{si,P}(T_P) &= -Q^o_{rxn,P} + \Sigma N_{i,R} h_{si,R}(T_R) \end{aligned}$$

With an initial guess of adiabatic flame temperature, $H_P(T_P)$ is determined. And if $H_P(T_P) < H_R(T_R)$, higher flame temperature is guessed. Repeating this process until the two closest temperatures are found. Finally, adiabatic flame temperature can be calculated using linear interpolation.

2.3.1.3 Method III: Adiabatic flame temperature as a result of different molar ratios of reactant mixture using software's (Python/Cantera/STANJAN)

The other term of interest on which adiabatic flame temperature depends is equivalence ratio which is denoted by ($\emptyset$) is the ratio of fuel to air corresponding to the actual conditions before combustion, to the fuel to air ratio that corresponds to the stoichiometric condition [16].

$$\emptyset = \frac{f}{f_s}, \quad \begin{Bmatrix} \emptyset < 1, \text{lean mixture} \\ \emptyset = 1, \text{stoichiometric mixture} \\ \emptyset > 1, \text{rich mixture} \end{Bmatrix} \qquad (2.12)$$

Where,

f = actual fuel-air ratio [-]

f_s = stoichiometric fuel-air ratio [-]

The method procedure stepwise to calculate adiabatic flame temperature are further discussed briefly in subchapter (3.4.2).

2.4 Terminal settling velocity

In a constant, non-fluctuating fluid, the velocity of a solid particle or droplet will gradually level off at an equilibrium value and that is the maximum value that a particle can reach. When moving in stagnant medium ($u_F = 0$), a particle or droplet is subjected to gravity will speed up or slow down to what is known as terminal settling velocity, V_t which is illustrated by Figure 2.7 below [18].

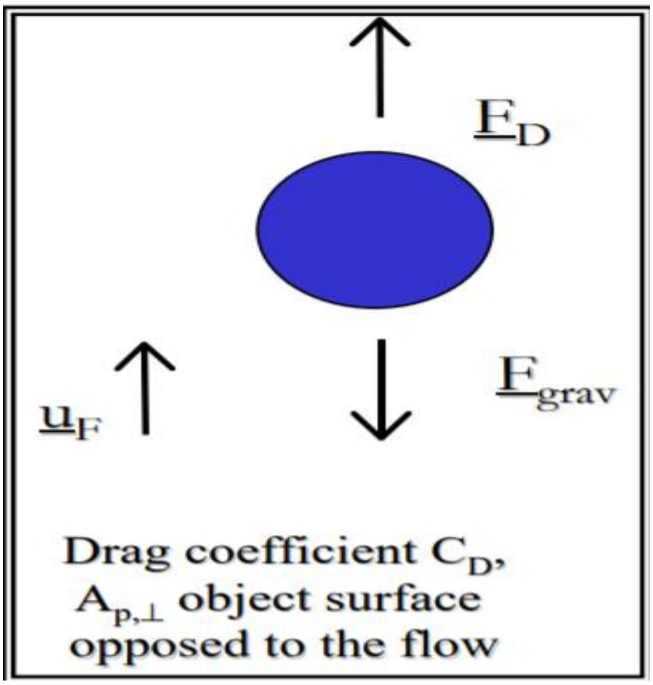


Figure 2.7: Forces on a spherical particle in a fluid flow [18]

The drag force (F_D) on a particle falling through a fluid is given by equation (2.13).

$$F_D = \frac{1}{2} C_D \rho_{gas} {v_t}^2 A_{p,proj} \tag{2.13}$$

where,

C_D = Drag coefficient [-]

v_t = settling velocity [m/s]

ρ_{gas} = density of fluid [kg/m^3]

$A_{p,proj}$ = Projected area of the particle [m^2]

The settling velocity can be determined using equation (2.14), considering spherical particles and settling in a Stokes regime, where relatively small particles are moving in a fluid and the Reynold's number is low i.e. Re<<<1 [18].

$$v_t = \frac{g D_p^2 (\rho_p - \rho_{gas})}{18\mu} \tag{2.14}$$

The settling of larger particles (Re>>1) is turbulent, and the terminal settling velocity can be determined using equations (2.15), (2.16) and (2.17).

Archimedes number: Ar = $\frac{\rho_{gas} \cdot (\rho_p - \rho_{gas}) \cdot g \cdot D_p^3}{\mu^2}$

Reynolds number: Re = $0.1334 \cdot Ar^{0.7016}$

$$\therefore \text{ Settling velocity: } V_t = \frac{Re \cdot \mu}{\rho_{gas} . D_p}$$

Where,

D_p= diameter of the particle [µm]

μ = dynamic viscosity of fluid [Pa.s]

2.5 Safety aspects of hydrogen

Although hydrogen fuel appears to be a promising option for the cement industry, it does come with its own set of challenges. In contrast to all other fuels, hydrogen has a wide range of flammability [19]. Accidents related to hydrogen, both small and large, have occurred as a result of improper handling or control. Leakage of hydrogen and the resulting fire are difficult to detect because gaseous hydrogen is colorless, odorless, and tasteless, and burns with a nearly invisible flame [20]. Its combustible nature may cause a fire, a minor explosion (deflagration), or a major explosion (denotation). Thus, introduction of a new energy carrier like hydrogen would be contingent on safety considerations.

2.5.1 Risk reduction by implementation of some safety measures

Employees, both trained and untrained, must be able to use hydrogen as a fuel with same level of safety [21]. Comprehensive safety program that address physical, chemical, and specific hazardous properties of hydrogen fuel should be included in training. All hydrogen systems and operations, regardless of quantity, must be hazard free by ensuring sufficient ventilation, designing, and operating to avoid leakage to eliminate possible ignition sources [22]. To adequately protect workers and equipment during hydrogen storage, handling, and use, safety valving and flow regulation should be installed [23].

3 Methods and Calculations

3.1 Mass and Energy Balance

Figure 3.1 below depicts the process flow diagram of specified system that implies combustion of hydrogen fuel in oxygen in a carbon dioxide rich atmosphere to pre-calcine the raw meal in the calciner. This new hypothetical system comprises water electrolyzer for the purpose to generate hydrogen and oxygen fuel by the use of electrical energy, pre-calciner where 210 tons of preheated meal at the temperature of 658°C enters per hour , CO_2 heat exchanger in an attempt to utilize the excess heat from the gases exiting from the calciner to heat up the air from the clinker cooler and condensor.

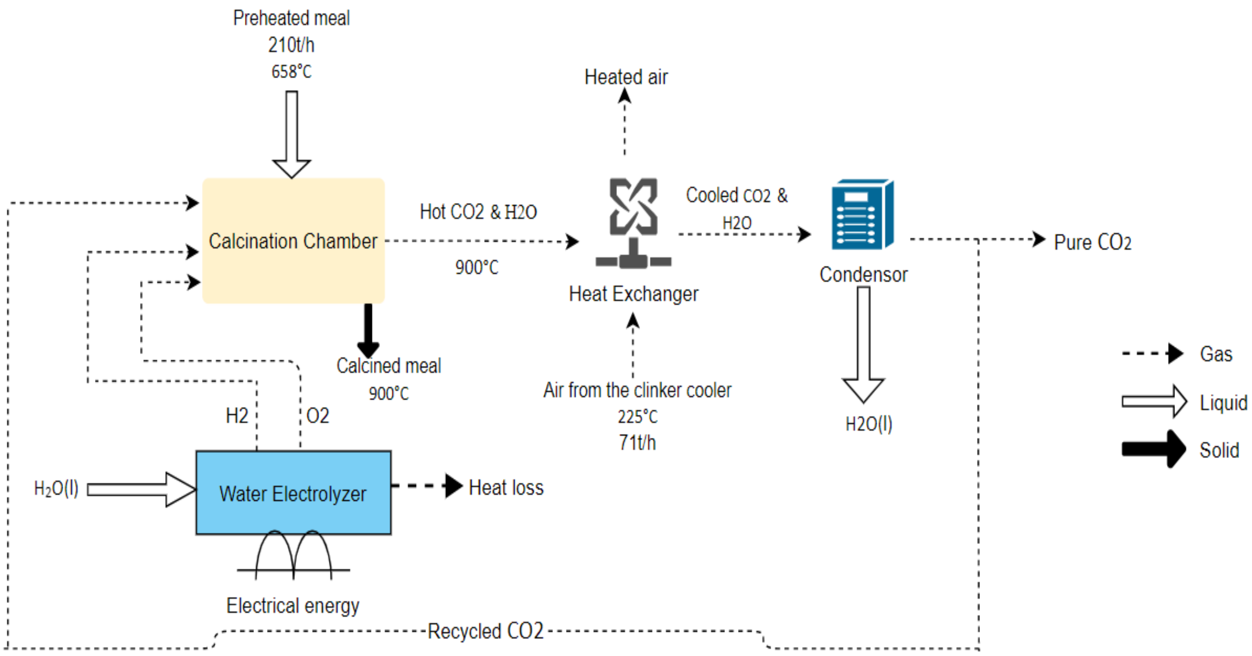


Figure3.1: Process flow diagram for the specified system of project

3.1.1 Mass Balance

Table 3.1 shows the design basis values for the mass balance.

Table 3.1: Mass balance design basis values [24]

Parameter	Design basis value	Unit
$\dot{m}_{PM}$	210	[t/h]
$w_{CaCO_3,PM}$	0.77	[kg/kg]
f_{pcal}	94%	[-]

3.1.1.1 Water Electrolyzer

The overall reactions in the water electrolyzer is:

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode (reduction): $2H^+(aq) + 2e^- \rightarrow H_2(g)$

To produce 1 mole of H_2 (or to consume 1 mole of H_2O), 2 moles of electrons are involved. This corresponds to the charge of:

$$Q = 2qN_0 \qquad 3.1$$

where,

q = elementary charge = 1.6×10^{-19} coulombs

N_0 = Avogadro's number = 6.023×10^{26} particles in one mole of any substance

Thus, the total rate of hydrogen production [kg/h] can be calculated by applying equation (3.2)

$$\dot{n}_{H_2} = \frac{NI}{Q} \cdot M_{H_2} \qquad 3.2$$

N = number of electrolysis cells

I = current withdrawn by each cell [coulombs/second]

M_{H_2}= molar mass of hydrogen [kg/mol]

To calculate the production rate of oxygen, we know that for each mole of H_2 produced from each mole of H_2O consumed, half a mole of O_2 are produced. And since the molecular mass of oxygen is 16 times greater than that of hydrogen, H_2 & O_2 gases are produced at the ratio of 8:1. Thus, O_2 production rate is calculated using equation (3.3).

$$\dot{m}_{O_2} = \dot{m}_{H_2} \cdot \frac{M_{O_2}}{M_{H_2}} \qquad 3.3$$

M_{o_2}= molar mass of oxygen [kg/mol]

Also, we know for each mole of H_2, one mole of H_2O is required. However, molecular mass of water is nine times higher than that of hydrogen. Hence, by applying equation (3.4), feed water consumption rate can be calculated.

$$\dot{m}_{H_2O} = \dot{m}_{H_2} \cdot \frac{M_{H_2O}}{M_{H_2}} \qquad 3.4$$

M_{H_2O}= molar mass of water [kg/mol]

3.1.1.2 Pre-Calciner

The mass balance equation for this specified system in a steady state condition in accordance to the figure 3.1 above is as follows: -

$$\dot{m}_{PM} = \dot{m}_{CO_2,m} + \dot{m}_{CMR} \qquad 3.5$$

where,

$\dot{m}_{PM}$ = mass flow rate of preheated meal [t/h]

$\dot{m}_{CMR}$ = mass flow rate of calcined meal [t/h]

$\dot{m}_{CO_2,m}$ = total CO_2 generated by meal in pre-calciner [t/h]

The total amount of CO_2 [t/h] in the calciner is the sum of CO_2 generated by meal and the recycled rate of CO_2 as per equation (3.6) below.

$$\dot{m}_{CO_2} = \dot{m}_{CO_2,m} + \dot{m}_{CO_2,r} \tag{3.6}$$

Recycle rate of CO_2 can be calculated using equation (3.7).

$$r_r = \frac{\dot{m}_{CO_2,r}}{\dot{m}_{CO_2,m}} \tag{3.7}$$

r_r = recycle ratio of CO_2

In order determine the total amount of CO_2 generated by meal, at first, we need to determine the total CO_2 content in the preheated meal that can be computed using equation (3.8).

$$w_{CO_2,PM} = w_{CaCO_3,PM} \cdot \frac{M_{CO_2}}{M_{CaCO_3}} \tag{3.8}$$

where,

M_{CO_2} = molecular mass of CO_2 [kg/mol]

M_{CaCO_3} = molecular mass of $CaCO_3$ [kg/mol]

After then, the total CO_2 generated by preheated meal ($\dot{m}_{CO_2,PM}$) can be computed using below equation (3.9).

$$\dot{m}_{CO_2,PM} = w_{CO_2,PM} \cdot \dot{m}_{PM} \tag{3.9}$$

And, to compute total amount of CO_2 generated by pre-calciner, equation (3.10) can be applied.

$$\dot{m}_{CO_2,m} = \dot{m}_{CO_2,PM} \cdot f_{pcal} \tag{3.10}$$

Adjusting equation (3.5), calcined meal rate can be calculated as follows.

$$\dot{m}_{CMR} = \dot{m}_{PM} - \dot{m}_{CO_2,m} \tag{3.11}$$

3.1.2 Energy Balance

Table 3.2 below shows the design basis values for the energy balance.

Table 3.2: Energy balance design basis values [24]

Parameter	Design basis value	Unit
n_{w-el}	80%	[-]

T_{ref}	25	[°C]
P_{ref}	1	[atm]
T_{PM}	658	[°C]
T_c	900	[°C]
H_c	-3.6	[MJ/kg$_{CO2}$]
$\Delta\ \mathrm{T}_{HEX,minimum}$	100	[K]
$T_{air,in}$	225	[°C]
$\dot{m}_{air}$	71	[t/h]
$T_{(CO_2\&H_2O),in}$	900	[°C]
$T_{CO_2,r}$	50	[°C]

3.1.2.1 Water Electrolyzer Energy Balance

To determine the total energy consumption of water electrolyzer with 100% efficiency, we know that higher heating value (HHV) of hydrogen is 142.18 MJ/kg [25] i.e. to produce 1 kg of hydrogen, we need to spend 142.18 MJ of energy which is equivalent to 39.49 kWh [1 kwh = 3.6 MJ]. i.e.

However, since the efficiency of water electrolyzer of our specified system is only 80% (design basis value), the total amount of electrical energy required to produce required amount of hydrogen fuel can be expressed as equation (3.12) below.

$$E_{n_{w-el}} = \frac{39.49}{n_{w-el}} \cdot \dot{m}_{H_2} \qquad 3.12$$

where,

n_{w-el} = efficiency of water electrolyzer [-]

$\dot{m}_{H_2}$ = required amount of hydrogen fuel for our specified system [t/h]

3.1.2.2 Calciner Energy Balance

In a steady state condition, the energy balance equation of calciner is as follows:

$$E_{in,c} + E_{gen,c} = E_{out,c} \qquad 3.13$$

where,

$E_{in,c}$ = Inlet energy [J/s]

$E_{gen,c}$ = Generated energy [J/s]

$E_{out,c}$ = Outlet energy [J/s]

And,

$$E_{in,c} = E_{PM} + E_{H_2} + E_{O_2} + E_{CO_2,r} \tag{3.14}$$

Inlet energy is determined by the sum of energy in a preheated meal (E_{PM}), hydrogen and oxygen fuel generated via water electrolysis (E_{H_2}&E_{O_2}) and recycled CO_2 ($E_{CO_2,r}$).

$$E_{PM} = \dot{m}_{PM} \cdot C_{p,PM} \cdot (T_{PM} - T_{ref}) \tag{3.15}$$

$$E_{H_2} = \dot{m}_{H_2} \cdot C_{p,H_2} \cdot (T_{H_2} - T_{ref}) \tag{3.16}$$

$$E_{O_2} = \dot{m}_{O_2} \cdot C_{p,O_2} \cdot (T_{O_2} - T_{ref}) \tag{3.17}$$

$$E_{CO_2,r} = \dot{m}_{CO_2,r} \cdot C_{p,CO_2,r} \cdot (T_{CO_2,r} - T_{ref}) \tag{3.18}$$

where,

$C_{p,PM}$ = specific heat at the constant pressure of preheated meal at T_{PM} [J/kg·K]

T_{PM} = temperature of preheated meal [K]

T_{ref} = reference temperature [K]

C_{p,H_2} = specific heat at the constant pressure of hydrogen fuel at T_{H_2} [J/kg·K]

T_{H_2} = temperature of hydrogen fuel entering the calciner [K]

C_{p,O_2} = specific heat at the constant pressure of oxygen fuel at T_{O_2} [J/kg·K]

T_{O_2} = temperature of oxgyen fuel entering the calciner [K]

$C_{p,CO_2,r}$ = specific heat at the constant pressure of CO_2 recycling back to calciner at $T_{CO_2,r}$ [J/kg·K]

$T_{CO_2,r}$ = temperature of CO_2 recycling back to the calciner [K]

To determine the required amount of hydrogen and oxygen fuel, let us consider 'n' which is adjustable parameter be the number of moles of CO_2 of our combustion setting followed by chemical reaction below:

$$H_2 + 0.5O_2 + nCO_2 \rightarrow H_2O + nCO_2 + heat$$

For every one mole of H_2 fuel combustion, we need to recycle 'n' moles of CO_2. Thus, mass flow of H_2 required in our system is determined by applying below equations (3.19), (3.20), (3.21).

$$\dot{n}_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{M_{CO_2}} \tag{3.19}$$

where,

$\dot{n}_{CO_2,r}$= molar flow rate of recycle CO_2 [mol/h]

$\dot{m}_{CO_2,r}$= mass flow rate of recycle CO_2 [t/h]

M_{CO_2}= molecular mass of CO_2 [kg/mol]

After then, molar flow rate of H_2 required can be achieved using equation (3.20).

$$\dot{n}_{H_2} = \frac{\dot{n}_{CO_2,r}}{n} \qquad 3.20$$

Therefore, mass flow rate of H_2 required for this system is computed as follows: -

$$\dot{m}_{H_2} = \dot{n}_{H_2} \cdot M_{H_2} \qquad 3.21$$

M_{H_2}= Molecular mass of hydrogen [kg/mol]

Similarly, for every half mole of O_2 combustion, we are recycling 'n' moles of CO_2. Thus, mass flow rate of O_2 required for this specified system ($\dot{m}_{O_2}$) is determined by applying below equations (3.22), (3.23).

$$\dot{n}_{O_2} = \frac{n_{O_2}}{n} \cdot \dot{n}_{CO_2,r} \qquad 3.22$$

$$\dot{m}_{O_2} = \dot{n}_{O_2} \cdot M_{O_2} \qquad 3.23$$

n_{O_2} = number of moles of oxygen from our combustion settling [mole]

M_{O_2}= molecular mass of oxygen [kg/mol]

Now, the generation of heat in a calciner ($E_{gen,c}$) consists of energy from pre-calcination i.e.

$$E_{gen,c} = E_{pre-cal}$$

$$E_{pre-cal} = \dot{m}_{CO_2,m} \cdot H_c \qquad 3.24$$

H_c= enthalpy of calcination [MJ/kg_{CO2}]

Outlet energy is the sum of energy in CO_2 and water vapor stream exiting from the calciner ($E_{CO_2,c}$&$E_{H_2O,c}$) and the meal that is calcined ($E_{meal,c}$) that can be computed using equations (3.26), (3.27), (3.28).

$$E_{out,c} = E_{meal,c} + E_{CO_2,c} + E_{H_2O,c} \qquad 3.25$$

$$E_{meal,c} = \dot{m}_{CMR} \cdot C_{p,meal,c} \cdot (T_c - T_{ref}) \qquad 3.26$$

$$E_{CO_2,c} = \dot{m}_{CO_2,m} \cdot C_{p,CO_2,c} \cdot (T_c - T_{ref}) \qquad 3.27$$

$$E_{H_2O,c} = \dot{m}_{H_2O} \cdot C_{p,H_2,O,c} \cdot (T_c - T_{ref}) \qquad 3.28$$

where,

T_c = calcination temperature [K]

$C_{p,meal,c}$ = specific heat at the constant pressure of calcined meal at T_c [J/kg·K]

$C_{p,CO_2,c}$= specific heat at the constant pressure of CO_2 at T_c [J/kg·K]

$C_{p,H_2,O,c}$ = specific heat at the constant pressure of water vapor at T_c [J/kg·K]

From our combustion setting, one mole of H_2O is produced when one mole of hydrogen is combusted with half mole of oxygen. Thus, mass flow rate of water vapor as a product of reaction ($\dot{m}_{H_2O}$) can be computed using below equations (3.29), (3.30).

$$n_{H_2} = n_{H_2O} \tag{3.29}$$

$$\dot{m}_{H_2O} = \dot{n}_{H_2O} \cdot M_{H_2O} \tag{3.30}$$

M_{H_2O} = molecular mass of water [kg/mol]

3.1.2.3 Heat Exchanger Energy Balance

The main purpose of heat exchanger in this specified system process flow is to utilize the excess heat from CO_2 gas and water vapor exiting from calciner to heat up the air from the clinker cooler back to preheater.

The outlet temperature of CO_2 gas and water vapor ($T_{(CO_2\&H_2O),out}$) stream from the heat exchanger can be determined from a condition where, heat capacity rate of air ($C \overset{\text{def}}{=} \dot{m}_{gas} \cdot C_{p,gas}$) is higher than that of gases exiting from the calciner. i.e.

$$T_{(CO_2\&H_2O),out} = T_{air,in} + \Delta \mathrm{T}_{HEX,minimum} \tag{3.31}$$

where,

$T_{air,in}$ = Inlet temperature of air from clinker cooler [K]

$\Delta \mathrm{T}_{HEX,minimum}$= Minimum temperature difference of heat exchanger [K]

The outlet temperature of the air can be determined using equation (3.32), if the heat capacity rate of air is lower than that of the gas streams exiting from calciner. i.e.

$$T_{air,out} = T_{(CO_2\&H_2O),in} - \Delta \mathrm{T}_{HEX,minimum} \tag{3.32}$$

where,

$T_{(CO_2+H_2O),in}$= Inlet temperature of gas streams exiting from calciner [K]

Finally, to compute the exit temperature of heated air stream from clinker cooler and gas stream from calciner exiting from heat exchanger, following heat balance equations (3.33) and (3.34) can be applied.

$$T_{air,exit} = T_{air,in} + \frac{(\dot{m}_{CO_2} \cdot C_{p,CO_2,HEX} + \dot{m}_{H_2O} . C_{p,H_2O,HEX})(T_{(CO_2\&H_2O),in} - T_{(CO_2+H_2O),exit})}{\dot{m}_{air} \cdot C_{p,air,HEX}} \tag{3.33}$$

$$T_{(CO_2\&H_2O),exit} = T_c - \frac{\dot{m}_{air} \cdot C_{p,air,HEX}(T_{air,exit} - T_{air,in})}{\dot{m}_{CO_2} \cdot C_{p,CO_2,HEX} + \dot{m}_{H_2O} \cdot C_{p,H_2O,HEX}} \tag{3.34}$$

where,

$C_{p,CO_2,HEX}$ = Specific heat at the constant pressure of CO_2 at the average temperature of the hot side [J/kg·K]

$C_{p,H_2O,HEX}$ = Specific heat at the constant pressure of H_2O at the average temperature of the hot side [J/kg·K]

$C_{p,air,HEX}$ = Specific heat at the constant pressure of air at the average temperature of the cold side [J/kg·K]

3.1.3 MATLAB for solving mass and energy balance

The mass and energy balance equations were solved using MATLAB R2021a and the respective code can be found in Appendix C. Some MATLAB functions were created to measure the properties of CaO, $CaCO_3$, CO_2, H_2O, and air at the necessary temperatures.

To compute the specific heat at constant pressure of $CaCO_3$[J/mol.K] at the desired temperature, below equation (3.35) has been implemented [17].

$$C_{p,CaCO_3} = a + bT + cT^{-2} \qquad 3.35$$

where,

$$a = 82.34e - 3\ , b = 4.975e - 5, c = -12.87e - 2 \qquad [273\text{K}<\text{T}>1033\text{K}]$$

This equation has been implemented as a MATLAB function to compute specfic heat of $CaCO_3$ i.e. $C_{p,CaCO_3}$. Similarly, using the correlations in [26], specific heat value of calcium oxide as a calcined meal at the temperature of 900°C ($C_{p,CaO}$) has been implemented in MATLAB.

Besides, to calculate the outlet temperatures of gases exiting from calciner (CO_2 and H_2O) and air in the heat exchanger, three MATLAB function have been created to compute the specific heat values $C_{p,CO_2,HEX}$[KJ/kg.K], $C_{p,H_2O,HEX}$[KJ/kg.K], and $C_{p,air,HEX}$[KJ/kg.K] at different temperatures. By applying Shomate equations (3.36), (3.37) [18] and equation (3.38) from [24], specific heat values were computed as below: -

$$C_{p,CO_2,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} \qquad 3.36$$

where,

$$t = \frac{T[K]}{1000}, a = 24.99735, b = 55.18696, c = -33.69137, d = 7.948387, e = -0.136638$$

$$C_{p,H_2O,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} \qquad 3.37$$

where,

$$t = \frac{T[K]}{1000}, a = 30.09200, b = 6.832514, c = 6.793435, d = -2.534480, e = 0.082139$$

$$C_{p,air,HEX} = mt + C \qquad 3.38$$

where,

$m = 2.14e - 4$, $C = 0.98$, and ‘t’ is in °C.

3.1.3.1 Results and Plotting

Below figures 3.2 and 3.3 shows the effect of CO_2 recycling rate on outlet temperature of CO_2 & water vapor exiting from heat exchanger and the outlet rate of CO_2 gas exiting from the calciner. The respective graphs were plotted using MATLAB program by solving mass and energy balance equations from subchapters 3.1.1 and 3.1.2. The average temperature of CO_2, water vapor, and air for heat exchanger were used as an input parameters for coding and plotting, while the temperature of the hydrogen and oxygen fuel entering the calciner and the combustion setting for the number of moles of CO_2 recycling were adjustable parameters.

Since hydrogen fuel is highly combustible and produces a very high flame temperature when combusted alone with oxygen fuel, the number of moles of CO_2 recycle in our combustion setting is critical in adjusting the desired flame temperature in the calciner. In addition, regarding the CO_2 recycle rate, this value must be determined based on the necessity to ensure that all particles within the calciner are entrained, which is further addressed in subchapter 3.3.

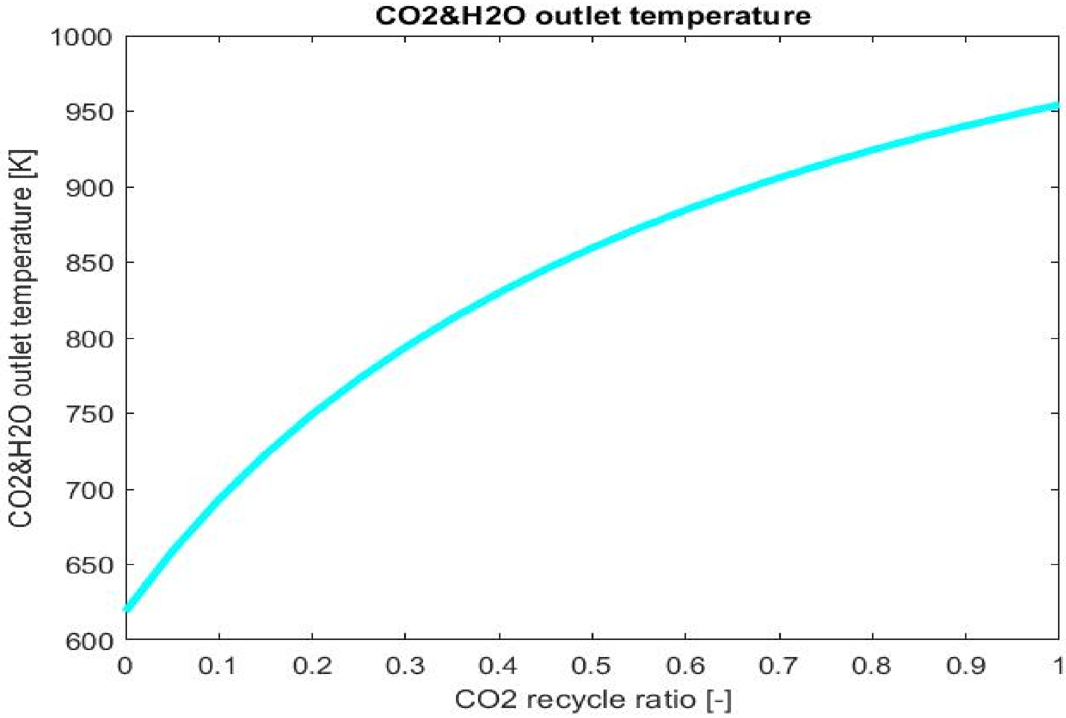


Figure3.2: Effect of CO_2 recycling rate on outlet temperature of CO_2 & water vapor exiting from heat exchanger

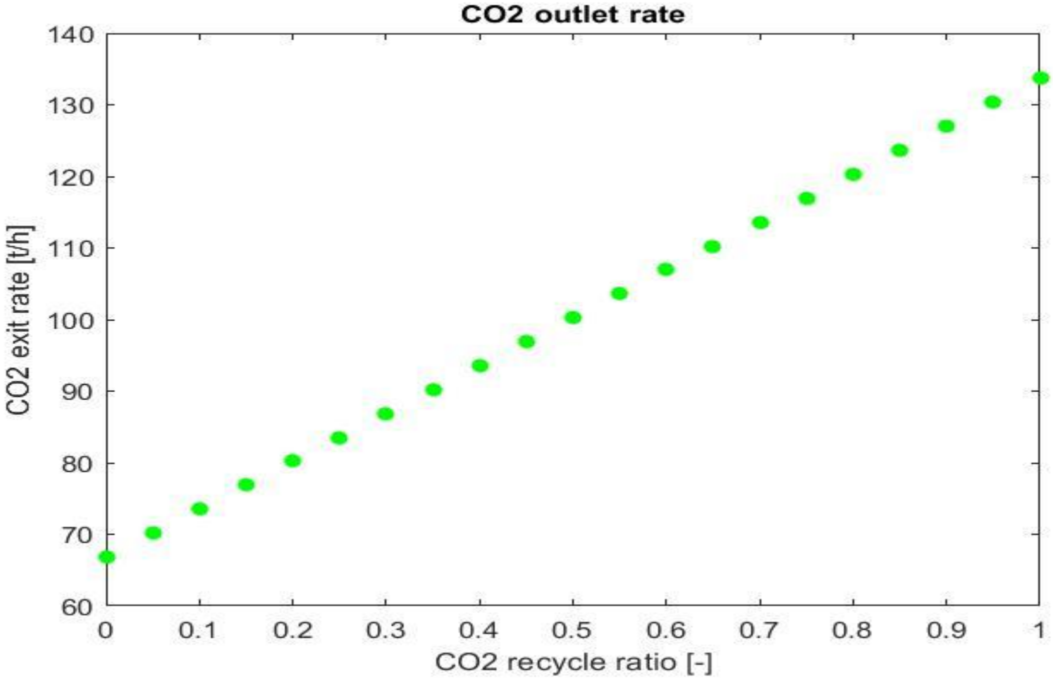


Figure3.3: Effect of CO_2 recycling rate on the outlet rate of CO_2 exiting from the calciner

3.2 Calculation Example for Mass and Energy Balance

Let us consider a recycle ratio of 0.1 i.e. 10% of CO_2 generated by the meal is recycle back to the calciner to be combusted with hydrogen and oxygen fuel generated via water electrolysis to calcine the meal. To solve mass and energy balance equations, all the design basis parameters are classified in table 3.1 and 3.2 above.

3.2.1 Mass Balance

To compute the total amount of CO_2 in the calciner ($\dot{m}_{CO_2,m}$) and mass flow rate of calined meal, first we need to determine $w_{CO_2,PM}, \dot{m}_{CO_2,PM}$ and $\dot{m}_{CO_2,m}$ as per equations (3.8),(3.9) &(3.10) by considering the values of M_{CO_2} & M_{CaCO_3} equal to 44.009×10^{-3} and 100.0869×10^{-3} [kg/mol] respectively.

$$w_{CO_2,PM} = w_{CaCO_3,PM} \cdot \frac{M_{CO_2}}{M_{CaCO_3}} = 0.77 \times \frac{44.009 \times 10^{-3}}{100.0869 \times 10^{-3}} = 0.3385$$

$$\dot{m}_{CO_2,PM} = w_{CO_2,PM} \cdot \dot{m}_{PM} = 0.3385 \times 210 = 71.1 \left[\frac{t}{h}\right]$$

$$\dot{m}_{CO_2,m} = \dot{m}_{CO_2,PM} \cdot f_{pcal} = 71.1 \times 0.94 = 66.83 \left[\frac{t}{h}\right]$$

With an assumption of recycle ratio of CO_2 as (r_r =0.1), mass flow rate of CO_2 recycle back to calciner ($\dot{m}_{CO_2,r}$) can be computed applying equation (3.7).

$$\dot{m}_{CO_2,r} = r_r \cdot \dot{m}_{CO_2,m} = 0.1 \times 66.83 = 6.68 \left[\frac{t}{h}\right]$$

Therefore, total amount of CO_2 in the calciner for our specified assumed system can be calculted using equation (3.6) while calcined meal rate can be computed using equation (3.11).

$$\dot{m}_{CO_2} = \dot{m}_{CO_2,m} + \dot{m}_{CO_2,r} = 66.83 + 6.68 = 73.51 \left[\frac{t}{h}\right]$$

$$\dot{m}_{CMR} = \dot{m}_{PM} - \dot{m}_{CO_2,m} = 210 - 66.83 = 143.17 \left[\frac{t}{h}\right]$$

3.2.2 Energy Balance

3.2.2.1 Water Electrolyzer and Calciner Energy Balance

Energy balance for our specified system can be computed using equation (3.13) as follows: -

$$E_{in,c} + E_{gen,c} = E_{out,c}$$

To calculate inlet energy in the system, equations (3.15),(3.16),(3.17) and (3.18) can be used.

$$E_{PM} = \dot{m}_{PM} \cdot C_{p,PM} \cdot (T_{PM} - T_{ref}) = 210 \times 1.26 \times 10^3 \times (658 - 25) \times \left(\frac{1000}{3600}\right)$$

$$= 46.53\ MJ/s$$

$$E_{CO_2,r} = \dot{m}_{CO_2,r} \cdot C_{p,CO_2,r} \cdot \left(T_{CO_2,r} - T_{ref}\right) = 6.58 \times 0.871 \times 10^3 \times (50 - 25) \times \left(\frac{1000}{3600}\right)$$
$$= 0.04\ MJ/s$$

$$E_{H_2} = \dot{m}_{H_2} \cdot C_{p,H_2} \cdot (T_{H_2} - T_{ref})$$

$$E_{O_2} = \dot{m}_{O_2} \cdot C_{p,O_2} \cdot (T_{O_2} - T_{ref})$$

Unknown values: $\dot{m}_{H_2}, \dot{m}_{O_2}, C_{p,H_2}$ & C_{p,O_2}

Computing $\dot{m}_{H_2}$; considering the values of M_{H_2} and M_{O_2}equal to 2.016×10^{-3} [kg/mol] and 31.998×10^{-3} [kg/mol] respectively.

Since we know the mass flow rate of CO_2 recycling and its molar mass, we can compute molar flow rate of CO_2 recyling back to calciner i.e.

$$\dot{n}_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{M_{CO_2}} = \frac{6.68}{44.009 \times 10^{-3}} = 151508.27\ \left[\frac{mol}{h}\right]$$

Assumption: Let us consider to adjust the desirable flame temperature to calcine the raw meal, for every one mole of H_2 and half mole of O_2, 1.75 mole of CO_2 is recycled back to caliner. i.e. (n=1.75). Thus, molar flow rate and mass flow rate of hydrogen required for the system can determined using equations (3.20) and (3.21).

$$\dot{n}_{H_2} = \frac{\dot{n}_{CO_2,r}}{n} = \frac{151508.27}{1.75} = 86576.159\ \left[\frac{mol}{h}\right]$$

$$\dot{m}_{H_2} = \dot{n}_{H_2} \cdot M_{H_2} = 86576.159 \times 2.016 \times 10^{-3} = 174.53\left[\frac{kg}{h}\right] = 0.174\left[\frac{t}{h}\right]$$

Computing $\dot{m}_{O_2}$;

Similarly, the required mass flow rate of oxygen in a system can be determined using equation (3.22) and (3.23).

$$\dot{n}_{O_2} = \frac{n_{O_2}}{n} \cdot \dot{n}_{CO_2,r} = \frac{0.5}{1.75} \times 151508.27 = 43288.077\ \left[\frac{mol}{h}\right]$$

$$\dot{m}_{O_2} = \dot{n}_{O_2} \cdot M_{O_2} = 43288.077 * 31.998 \times 10^{-3} = 1385.13\left[\frac{kg}{h}\right] = 1.385\left[\frac{t}{h}\right]$$

Let us consider the temperature of hydrogen and oxygen fuel enetering the calciner is 30°C .At this temperature, determing the specific heat at constant pressure of H_2 and O_2 (C_{p,H_2} & C_{p,O_2}) using Shomate equation, we get

$$C_{p,H_2} = 28.64 \times 10^3 \left[\frac{J}{Kg.K}\right]$$

$$C_{p,O_2} = 0.77 \times 10^3 \left[\frac{J}{Kg.K}\right]$$

Inserting all the determined values ($\dot{m}_{H_2}, \dot{m}_{O_2}, C_{p,H_2}$ & C_{p,O_2}) in equations(3.17) and (3.18), we get

$$E_{H_2} = 0.1745 \times 28.64 \times 10^3 \times (30 - 25) \times \left(\frac{1000}{3600}\right) = 0.00694\ MJ/s$$

$$E_{O_2} = 1.385 \times 0.77 \times 10^3 \times (30 - 25) \times \left(\frac{1000}{3600}\right) = 0.00148\ MJ/s$$

Therefore,
Total inlet energy can be calculated using equation (3.14).

$$E_{in,c} = E_{PM} + E_{H_2} + E_{O_2} + E_{CO_2,r} = 46.53 + 0.00694 + 0.00148 + 0.04$$
$$= 46.578\ MJ/s$$

Equations (3.26), (3.27) and (3.28) can be applied to calculate outlet energy of the system.

$$E_{meal,c} = \dot{m}_{CMR} \cdot C_{p,meal,c} \cdot \left(T_c - T_{ref}\right) = 143.17 \times 0.935 \times 10^3 \times (900 - 25) \times \left(\frac{1000}{3600}\right)$$
$$= 32.53\ MJ/s$$

$$E_{CO_2,c} = \dot{m}_{CO_2,m} \cdot C_{p,CO_{2},c} \cdot \left(T_c - T_{ref}\right) = 73.51 \times 1.27 \times 10^3 \times (900 - 25) \times \left(\frac{1000}{3600}\right)$$
$$= 22.69\ MJ/s$$

$$E_{H_2O,c} = \dot{m}_{H_2O} \cdot C_{p,H_{2,}O,c} \cdot (T_c - T_{ref})$$

Equation (3.30) and shomate equation (3.37) can be used to calculate $\dot{m}_{H_2O}$ and $C_{p,H_{2,}O,c}$ considering the values of M_{H_2O} equal to 18×10^{-3} [kg/mol].

$$\dot{m}_{H_2O} = \dot{n}_{H_2O} \cdot M_{H_2O} = 86576.159 \times 18 \times 10^{-3} = 1558.3 \left[\frac{kg}{h}\right] = 1.558 \left[\frac{t}{h}\right]$$

$$C_{p,H_2O,c} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} = 2.4 \times 10^3 \left[\frac{J}{Kg.K}\right]$$

Inserting all these values in equation (3.28) and (3.25), total outlet energy can be calculated as follows: -

$$E_{H_2O,c} = \dot{m}_{H_2O} \cdot C_{p,H_{2,}O,c} \cdot \left(T_c - T_{ref}\right) = 1.558 \times 2.4 \times 10^3 \times (900 - 25) \times \left(\frac{1000}{3600}\right)$$
$$= 0.909\ MJ/s$$

$$E_{out,c} = E_{meal,c} + E_{CO_2,c} + E_{H_2O,c} = 32.53 + 22.69 + 0.909 = 56.129\ MJ/s$$

Now,
Determining total generated energy using equation (3.24), we get

$$E_{gen,c} = E_{pre-cal} = \dot{m}_{CO_2,m} \cdot H_c = 66.83 \times (-3.6 \times 10^6) \times \left(\frac{1000}{3600}\right) = -66.830\ MJ/s$$

Total electrical energy consumption by the water electrolyzer with the efficiency of 80% (design basis value) can be calculated by applying equation (3.12).

$$E_{n_{w-el}} = \frac{39.49}{n_{w-el}} \cdot \dot{m}_{H_2} = \frac{39.49}{0.80} \times 0.1745 \times 1000 = 0.00861\ MW$$

3.2.2.2 Heat Exchanger Energy Balance

Let us consider input parameters, the average temperature of CO$_2$ and water vapor side are; $T_{ave,CO_2} = 900$ K & $T_{ave,H_2O} = 900$ K. So, the specific heat at constant pressure of the gases exiting from the calciner at the respective assumed avaerage temperature can be calculated using equation (3.36) and (3.37).

$$C_{p,CO_2,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} = 1.204 \times 10^3\ \left[\frac{J}{Kg.K}\right]$$

$$C_{p,H_2O,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} = 2.22 \times 10^3\ \left[\frac{J}{Kg.K}\right]$$

Also, assuming the average temperature of airstream to be $T_{ave,air} = 600$ K. At this temperature specific heat at constant pressure of air can be computed using equatiom (3.38).

$$C_{p,air,HEX} = mt + C = 1.05 \times 10^3\ \left[\frac{J}{Kg \cdot K}\right]$$

Design Basis Values:

$\Delta T_{HEX,minimum} = 100$ K

$T_{air,in} = 225$°C = 498.15 K

$T_{(CO_2\&H_2O),in} = 900$°C = 1173.15 K

Heat capacity rate of air (C_{air}) is lower than that of the sum of heat capacity rate of gases exiting from calciner $(C_{CO_2} + C_{H_2O})$. i.e.

$$C_{air} = \dot{m}_{air} \cdot C_{p,air,HEX} < (C_{CO_2} + C_{H_2O}) = (\dot{m}_{CO_2} \cdot C_{p,CO_2,HEX} + \dot{m}_{H_2O} \cdot C_{p,H_2O,HEX})$$

Therefore, Outlet temperature of air can be calculated using equation (3.32).

$$T_{air,out} = T_{(CO_2\&H_2O),in} - \Delta T_{HEX,minimum} = 1173.15 - 100 = 1073.15\ K$$

So, the average temperature of air stream side is: -

$$T_{ave,air} = \frac{T_{air,in} + T_{air,out}}{2}$$

$$= \frac{498.15 + 1073.15}{2}$$

$$= 785.65\ K$$

Now,

Calculating the specific heat at constant pressure of air at the computed average temperature of airstream side by applying equation (3.38), we get

$$C_{p,air,HEX} = mt + C = 1.0897 \times 10^3\ \left[\frac{J}{Kg.K}\right]$$

Hence, the exit temperature of gases exiting from heat exchanger can be determined applying equation (3.34).

$$T_{(CO_2\&H_2O),exit} = T_c - \frac{\dot{m}_{air} C_{p,air,HEX}\left(T_{air,exit} - T_{air,in}\right)}{\dot{m}_{CO_2} C_{p,CO_2,HEX} + \dot{m}_{H_2O} C_{p,H_2O,HEX}}$$

$$= 1173.15 - \frac{71 \times 1.0897 \times (1073.15 - 498.15)}{(73.51 \times 1.204) + (1.558 \times 2.22)}$$

$$= 687.5\ K$$

Now, the average temperature of the CO_2 and $H_2O_{(\text{water vapor})}$ side can be calculated as: -

$$T_{ave,CO_2,H_2O} = \frac{T_{(CO_2\&H_2O),in} + T_{(CO_2\&H_2O),exit}}{2}$$

$$= \frac{1173.15 + 687.5}{2}$$

$$= 930.3\ K$$

Specific heat at constant pressure of the gases ($C_{p,CO_2,HEX}$ & $C_{p,H_2O,HEX}$) at the respective average temperature is calculated using the Shomate equations (3.36) and (3.37) as before.

$$C_{p,CO_2,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} = 1.215 \times 10^3\ \left[\frac{J}{Kg\cdot K}\right]$$

$$C_{p,H_2O,HEX} = a + bt + ct^2 + dt^3 + \frac{e}{t^2} = 2.244 \times 10^3\ \left[\frac{J}{Kg\cdot K}\right]$$

Exit temperature of combined CO_2 and $H_2O_{(\text{water vapor})}$ gases from the heat exchanger is calculated again applying equation (3.34).

$$T_{(CO_2\&H_2O),exit} = T_c - \frac{\dot{m}_{air} \cdot C_{p,air,HEX} \cdot \left(T_{air,exit} - T_{air,in}\right)}{\dot{m}_{CO_2} \cdot C_{p,CO_2,HEX} + \dot{m}_{H_2O} \cdot C_{p,H_2O,HEX}}$$

$$= 1173.15 - \frac{71 \times 1.0897 \times (1073.15 - 498.15)}{(73.51 \times 1.215) + (1.558 \times 2.244)}$$

$$= 692.87\ K$$

The similar procedure has to be repeated until we find the minimum temperature difference between the steps. From graph, we found the exit temperature of gases exiting from heat exchanger at the recycle ratio of 0.1 as $T_{(CO_2\&H_2O),exit} = 692.973\ K$.

3.3 Velocities Calculation: Particles Entrainment Inspection

The terminal settling velocity of particles settling in a calciner and the velocity of gases present in the calciner during the process flow are important characteristics to determine whether or not the raw meal is completely entrained from the calciner. The previous experience from full-scale calciner system is that the gas velocity should be in the order of (5-15) m/s to ensure entrainment of all particles [24].

3.3.1 Terminal Settling Velocity based on maximum particle size

The terminal settling velocity for the largest particle size i.e. 1000 µm settling in CO_2 and H_2O streams at the temperatures of 50°C and 900°C has been computed using the literature and formulae from sub-chapter (2.4). Value of density of (raw meal) limestone is 2711 kg/m^3 [28].

Calculation Example: Assuming settling in the stokes regime (i.e. relatively small particles, having $Re<<1$),

Terminal settling velocity of spherical particles is given by.

$$V_t = \frac{g \cdot D_p^2 \cdot (\rho_p - \rho_{gas})}{18 \cdot \mu}$$

Case I: For CO_2 gas at T = 50°C,

Density of gas (ρ_{gas}) = 1.643 kg/m^3

Dynamic viscosity (µ) = 1.614× 10^{-5} Pa·s

Now,

$$V_t = \frac{9.81 \times (1000 \times 10^{-6})^2 \times (2711 - 1.643)}{18 \times 1.614 \times 10^{-5}}$$

$$= 91.48\ m/s$$

Checking if Re>>1.

$Re = \frac{\rho_{gas} V_t D_p}{\mu} = \frac{1.643 \times 91.48 \times 1000 \times 10^{-6}}{1.614 \times 10^{-5}}$ = 9212.36 >>>1. Hence, the settling is turbulent.

Appling following equations to determine particle turbulent settling velocity,

Archimedes number: Ar = $\frac{\rho_{gas} \cdot (\rho_p - \rho_{gas}) \cdot g \cdot D_p^3}{\mu^2}$

Reynolds number: Re = $0.1334 \cdot Ar^{0.7016}$

Settling velocity: $V_t = \frac{Re \cdot \mu}{\rho_{gas} \cdot D_p}$

Substituting values in an equations, we get

Terminal settling velocity(V_t) = 6.06 *m/s*

Case II: For CO_2 gas at T = 900°C,

Density of gas (ρ_{gas}) = 0.45152 kg/m^3

Dynamic viscosity (μ) = 4.60× 10^{-5} Pa.s

Now,

$$V_t = \frac{9.81 \times (1000 * 10^{-6})^2 \times (2711 - 0.45152)}{18 \times 4.60 \times 10^{-5}}$$

= 32.11 *m/s*

Checking if Re>>1.

$Re = \frac{\rho_{gas} V_t D_p}{\mu} = \frac{0.45152 \times 32.11 \times 1000 \times 10^{-6}}{4.60 \times 10^{-5}}$ = 315.22 >>>1. Hence, the settling is turbulent.

Appling following equations to determine particle turbulent settling velocity,

Archimedes number: Ar = $\frac{\rho_{gas} \cdot (\rho_p - \rho_{gas}) \cdot g \cdot D_p^3}{\mu^2}$

Reynolds number: Re = 0.1334 · $Ar^{0.7016}$

Settling velocity: $V_t = \frac{Re \cdot \mu}{\rho_{gas} \cdot D_p}$

Substituting values in an equations, we get

Terminal settling velocity = 5.84 *m/s*

Case III: For H_2O gas at T = 900°C,

Density of gas (ρ_{gas}) = 0.2701 kg/m^3

Dynamic viscosity (μ) = 1.06× 10^{-5}Pa.s

Now,

$$V_t = \frac{9.81 \times (1000 \times 10^{-6})^2 \times (2711 - 0.2701)}{18 \times 1.06 \times 10^{-5}}$$

= 139.37 *m/s*

Checking if Re>>1.

$Re = \frac{\rho_{gas} V_t D_p}{\mu} = \frac{0.2701 \times 139.38 \times 1000 \times 10^{-6}}{1.06 \times 10^{-5}}$ = 3551.3 >>>1. Hence, the settling is turbulent.

Appling following equations to determine particle turbulent settling velocity, Archimedes number: Ar = $\frac{\rho_{gas} \cdot (\rho_p - \rho_{gas}) \cdot g \cdot D_p^3}{\mu^2}$

Reynolds number: Re = $0.1334 \cdot Ar^{0.7016}$

Settling velocity: V_t = $\frac{Re \cdot \mu}{\rho_{gas} \cdot D_p}$

Substituting values in an equations, we get

Terminal settling velocity = 12.31 *m/s*

3.3.2 Velocity of Gases in the Calciner

Assumption: Recycle ratio of CO_2, $r_r = 0.1$

Diameter of calciner (design basis value) = 3.74 m

Therefore,

$$\text{Cross sectional area}, A = \pi r^2 = 10.98 \text{ m}^2$$

Now,

Gas flow in calciner is the sum of:

i. CO_2 generated by calciner ($\dot{m}_{CO_2,m}$) = 66.83 t/h
ii. Recycled rate of CO_2 back to calciner ($\dot{m}_{CO_2,r}$) = 6.68 t/h
iii. The water vapor produced by combustion reaction($\dot{m}_{H_2O}$) = 1.55 t/h

Unit conversion for (t/h) to (mol/h)

- 1 ton = 1000 kg
- 1m^3 = 1000 liter
- One mole of CO_2 = 44 g
- One mole of water vapor = 18g

Then, determining the molar flow rate of the gases in the calciner:

- Molar flow rate of CO_2 gas generated by calciner ($\dot{n}_{CO_2,m}$)can be calculated as,

$$\dot{n}_{CO_2,m} = \frac{\dot{m}_{CO_2,m}}{44} = 1518863.636 \text{ [mol/h]}$$

- Molar flow rate of CO_2 recycling back to calciner can be calculated as,

$$\dot{n}_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{44} = 151818.18 \text{ [mol/h]}$$

- Molar flow rate of water vapor($\dot{n}_{H_2O}$) can be calculated as,

$$\dot{n}_{H_2O} = \frac{\dot{m}_{H2O}}{18} = 86111.11 \text{ [mol/h]}$$

Now, determining the volumetric flow rate of the respective gases in the calciner applying ideal gas law.

$$P\dot{V} = \dot{n}RT$$

where,

Pressure (P) = 1 atm

Universal gas constant (R)= 0.08206 $\left[\frac{\mathrm{atm \cdot L}}{\mathrm{gmol \cdot K}}\right]$,

i. Volumetric flow rate of CO_2 gas at 900°C generated by calciner is: -

$$\dot{V}_{CO_2,m} = \frac{\dot{n}_{CO_2,m}RT}{P} = \frac{1518863.636 \times 0.08206 \times 1173.15}{1} = 40.61\ m^3/s$$

ii. Volumetric flow rate of recycling CO_2 gas back to calciner is: -

$$\dot{V}_{CO_2,r} = \frac{\dot{n}_{CO_2,r}RT}{P} = \frac{151818.18 \times 0.08206 \times 1173.15}{1} = 4.06\ m^3/s$$

iii. Volumetric flow rate of water vapor produced by combustion reaction in calciner is: -

$$\dot{V}_{H_2O} = \frac{\dot{n}_{H_2O}RT}{P} = \frac{86111.11 \times 0.08206 \times 1173.15}{1} = 2.30\ m^3/s$$

Therefore,

Total volumetric flow rate of gases in a calciner = $\dot{V}_{CO_2,m} + \dot{V}_{CO_2,r} + \dot{V}_{H_2O}$ = 46.97 m^3/s

∴Velocity of gas in the calciner (V_{gas}) = $\frac{Total\ volumetric\ flow\ rate}{Cross\ sectional\ area} = \frac{46.97}{10.98}$ = 4.278 *m/s*

The velocity of gas in the calciner must be in the range of (5-15) m/s for the particles in the calciner to be completely entrained, according to the full scale calciner system experience. Following procedures in the system can be implemented to get the desired velocity as follows:

Option I: Increasing the recycle ratio of CO_2.

Option II: Constructional changes of calciner with a smaller diameter than the design basis value i.e. (3.74 m).

3.4 Method and Calculation Example of AFT

This chapter includes the methods and calculation examples of adiabatic flame temperature as a result of modified cement kiln system i.e. hydrogen combustion in oxygen in a carbon dioxide rich atmosphere and regular cement kiln system that implies coal/air combustion to calcine the raw meal in a subchapter (3.4.1) and (3.4.2).

3.4.1 Calculation Example of AFT using average C_p value

3.4.1.1 H_2 Combustion in O_2 in a CO_2 Rich Atmosphere

The combustion stoichiometry is: -

$$2H_2 + O_2 + CO_2 \rightarrow 2H_2O + CO_2$$

First, computing heat of combustion using equation (2.5).

$$Q^o_{rxn,P} = \sum N_{i,P}\Delta h^o_{i,P} - \sum N_{i,R}\Delta h^o_{i,R}$$

From thermodynamics physical property table (Appendix D),

$\Delta h^0{}_{H_2O(g)} = -241.83$ [kJ/mol]

$\Delta h^0{}_{CO_2(g)} = -393.52$ [kJ/mol]

$\Delta h^0{}_{H_2(l)} = 0$ [kJ/mol]

$\Delta h^0{}_{H_2(l)} = 0$ [kJ/mol]

Inserting the values, we get

$$Q^o_{rxn,P} = [(2 \times (-241.83) + (1 \times (-393.52)) - (2 \times 0) + (2 \times 0) + (2 \times (-393.52))]$$
$$= -483.66\, kJ$$

Now,

Assuming a constant (average) C_p at 1500 K, determining specific heat at constant pressure of product species i.e. $C_{p,H_2O}(1500K)$ &$C_{p,CO_2}(1500K)$ using physical property table, we get

$C_{p,H_2O}(1500K) = 0.0467$ [kJ/mol·K]

$C_{p,CO_2}(1500K) = 0.0584$ [kJ/mol·K]

Product temperature is then calculated using equation (2.8).

$$T_p = T_r + \frac{-Q^o_{rxn,P}}{\Sigma N_{i,P}\cdot c_{Pi}} = 298.15 + \frac{-(-483.66)}{(2\times0.0467)+(1\times0.0584)}$$
$$= 3484.3\, K$$

Now, the average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 3484.3}{2} = 1891.2\, K$$

This indicates that the initial assumption of $T_{ave} = 1500$ K was low. Thus, evaluating the specific heat and flame temperature using the new average temperature i.e. $T_{ave} = 1891.2\, K$.

$C_{p,H_2O}(1891.2K) = 0.0493$ [kJ/mol·K]

$C_{p,CO_2}(1891.2K) = 0.0609$ [kJ/mol·K]

$$T_p = T_r + \frac{-Q^o_{rxn,P}}{\Sigma N_{i,P}\cdot c_{Pi}} = 298.15 + \frac{-(-483.66)}{(2\times0.0493)+(1\times0.0609)}$$
$$= 3330.5\, K$$

The average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 3330.5}{2} = 1814.3\ K$$

Again, Computing the specific heat and flame temperature using the new average temperature i.e. $T_{ave} = 1814.3$ K.

$C_{p,H_2O}(1814.3\ K) = 0.0489$ [kJ/mol·K]

$C_{p,CO_2}(1814.3\ K) = 0.0600$ [kJ/mol·K]

$$T_p = T_r + \frac{-\,Q^{o}_{rxn,P}}{\Sigma\, N_{i,P} \cdot c_{Pi}} = 298.15 + \frac{-(-483.66)}{(2\times0.0489)+(1\times0.0600)}$$

$$= 3361.2\ K$$

The average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 3361.2}{2} \approx 1829.7\ K$$

Since, the change in average temperature is in the order of less than 20 K. The final adiabatic flame temperature of the combustion reaction is ≈ 3361.2 K.

3.4.1.2 Coal/Air Combustion

Table 3.3 below depicts the chemical composition of coal which is specifically used by NORCEM Brevik AS for the cement production and calculation of its pseudo-chemical formula [29].

Table 3.3: Coal composition and its chemical formula [29]

Element	**Wt** %		$^{mol}/_{100\ gm}$	$^{mol}/_{mol\ C}$
C	72.2	÷ 12	6.0167	1
H	4	÷ 1	4	0.6648
O	5.7	÷ 16	0.3562	0.0592
S	1.2	÷ 32	0.0375	0.0062
N	1.6	÷ 14	0.143	0.0237
H_2O	1.8	÷ 18	0.1	0.0166
Ash	13.5			2.243 g/mol C

Therefore, pseudo-chemical formula of coal is as follows: -

$CH_{0.6648}N_{0.0237}S_{0.0062}O_{0.0592}(H_2O)_{0.0166}$

$= CH_{0.6980}N_{0.0237}S_{0.0062}O_{0.0758}$

Now, determining the stoichiometric combustion reaction of the specific coal/air.

$$CH_{0.6980}N_{0.0237}S_{0.0062}O_{0.0758} + \alpha(\, O_2 + 3.78N_2) \\ \rightarrow\ CO_2 + \frac{0.6980}{2}\, H_2O + 0.0062SO_2 + \left(3.78\alpha + \frac{0.0237}{2}\right) N_2$$

Where,

$\alpha = x + \frac{y}{4} + z - \frac{a}{2}$, $(C_xH_yN_zSO_a)$ (Refer to [25])

$$= 1 + \frac{0.6980}{4} + 0.0237 - \frac{0.0758}{2} = 1.16$$

Hence,

The combustion stoichiometry is;

$$CH_{0.6980}N_{0.0237}S_{0.0062}O_{0.0758} + 1.16(\, O_2 + 3.78N_2) \\ \rightarrow\ CO_2 + 0.349H_2O + 0.0062SO_2 + 4.396N_2$$

Using constant (average) C_p method and applying equation (2.9) to compute combustion product temperature (T_p).

$$T_p = T_r + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\Sigma\, N_{i,P}\cdot c_{Pi}}$$

where,
T_r = 298.15 K
N_{fuel} = 1 [mol]
M_{fuel} = molecular mass of coal = 14.525 [g/mol]

Assumption: Let us consider the lower heating value of this specific coal to be 12500 btu/lb which is equivalent to 29.07 MJ/kg.

Now, assuming a constant (average) C_p at 1500 K and determining specific heat at constant pressure of product species i.e. C_{p,H_2O}, C_{p,CO_2}, C_{p,SO_2}, & C_{p,N_2} using physical property table, we get

$C_{p,H_2O}(1500K) = 0.0467$ [kJ/mol·K]

$C_{p,CO_2}(1500K) = 0.0584$ [kJ/mol·K]

$C_{p,SO_2}(1500K) = 0.0559$ [kJ/mol·K]

$C_{p,N_2}(1500K) = 0.0350$ [kJ/mol·K]

Thus, Product temperature is: -

$$T_p = T_r + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\Sigma\, N_{i,P}\cdot c_{Pi}}$$
$$= 298.15 + \frac{29.07\times10^{3}\times1\times14.525\times10^{-3}}{(1\times0.0584)+(0.349\times0.0467)+(0.0062\times0.0559)+(4.396\times0.0350)}$$
$$= 2143.6\ K$$

Now, the average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 2143.6}{2} = 1220.8\ K$$

This indicates that the initial assumption of $T_{ave} = 1500$ K was high. Thus, evaluating the specific heat and flame temperature using the new average temperature i.e. $T_{ave} = 1220.8$ K.

$C_{p,H_2O}(1220.8K) = 0.0434$ [kJ/mol·K]

$C_{p,CO_2}(1220.8K) = 0.0564$ [kJ/mol·K]

$C_{p,SO_2}(1220.8K) = 0.0553$ [kJ/mol·K]

$C_{p,N_2}(1220.8K) = 0.0336$ [kJ/mol·K]

$$T_p = T_r + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\Sigma\, N_{i,P}\cdot c_{Pi}}$$
$$= 298.15 + \frac{29.07\times10^{3}\times1\times14.525\times10^{-3}}{(1\times0.0564)+(0.349\times0.0434)+(0.0062\times0.0553)+(4.396\times0.0336)}$$
$$= 2220.9\ K$$

The average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 2220.9}{2} = 1259.5\ K$$

Again, Computing the specific heat and flame temperature using the new average temperature i.e. $T_{ave} = 1259.5$ K.

$C_{p,H_2O}(1259.5K) = 0.0442$ [kJ/mol·K]

$C_{p,CO_2}(1259.5K) = 0.0571$ [kJ/mol·K]

$C_{p,SO_2}(1259.5K) = 0.0555$ [kJ/mol·K]

$C_{p,N_2}(1259.5K) = 0.0339$ [kJ/mol·K]

$$T_p = T_r + \frac{\text{LHV}\cdot N_{fuel}\cdot M_{fuel}}{\Sigma\, N_{i,P}.c_{Pi}}$$
$$= 298.15 + \frac{29.07\times10^{3}\times1\times14.525\times10^{-3}}{(1\times0.0571)+(0.349\times0.0442)+(0.0062\times0.0555)+(4.396\times0.0339)}$$
$$= \ 2201.04\ K$$

The average temperature of reactants and products is: -

$$T_{ave} = \frac{298.15 + 2201.04}{2} \approx 1249.6\ K$$

Since, the change in average temperature is in the order of less than 20 K. The final adiabatic flame temperature of the coal/air combustion reaction is ≈ 2201.04 K.

3.4.2 Calculation of Adiabatic Flame Temperature using PYTHON

The effect of equivalence ratio on adiabatic flame temperature assuming hydrogen combustion in oxygen in a carbon dioxide rich atmosphere in a constant pressure calciner chamber was investigated using Python programming. The following sub-chapters (3.4.2.1),(3.4.2.2) and (3.4.2.3) deals with the python coding procedure and results of plotting.

3.4.2.1 Python Code for Calculation

To evaluate the effect of equivalence ratio on adiabatic flame temperature, code was developed in spyder (Python 2.7) which is attached in Appendix E. The coding approach is discussed furthermore step by step.

Step 1:

All the required packages were imported.

Step 2:

Enthalpy function, named ‘h’ was defined, taking temperature and temperature coefficient values as input. To obtain enthalpy, NASA polynomials have been used which is attached in Appendix F.

$H = [a1 + a2\cdot (T/2) + a3\cdot (T^2/3) + a4\cdot (T^3/4) + a5\cdot (T^4/5) + a6/T) \cdot R\cdot T$ (3.40)

Where,

a1, a2, a3, a4, a5, a6 = temperature coefficients.

Temperature coefficients were taken from NASA thermodynamics file, where the first seven coefficients are for high temperature range and were defined for the combustion product species whereas last seven coefficients are for low temperature range and were defined for reactant species.

Step 3:

Another function named ‘f ‘was defined, that takes T and phi (equivalence ratio) as inputs.

To find enthalpies and number of moles of reactants and products, equation obtained from lean hydrogen combustion equation was used as follows:

Enthalpy of reactant (H_r): $H_{H_2} + \frac{1}{2}\ H_{O_2} + \frac{1}{\emptyset}\ H_{CO_2}$ (3.41)

Enthalpy of product (H_p): $H_{H_2O} + \frac{1}{\emptyset}\ H_{CO_2}$ (3.42)

The enthalpies for different species in reactants and products were obtained by running the function for enthalpy by providing the temperature and thermodynamic temperature coefficients.

Step 4

Derivative of the function was defined as f-prime for conducting iteration and root finding using Newton Raphson method with an initial guess of final temperature as a input parameter. lets say, (T_{p1}).

3.4.2.2 Results of Python Code to determine AFT with dependency on Equivalence Ratio

Figure 3.4 depicts the effect of equivalence ratio on adiabatic flame temperature of our combustion mixture, which contains H_2, O_2 and CO_2. The main goal of evaluating flame temperature based on different equivalence ratios is to adjust our combustion setting that is suitable for our specified system by comparing it to the flame temperature as a result of coal/air combustion used in regular cement kiln system to calcine the raw meal.

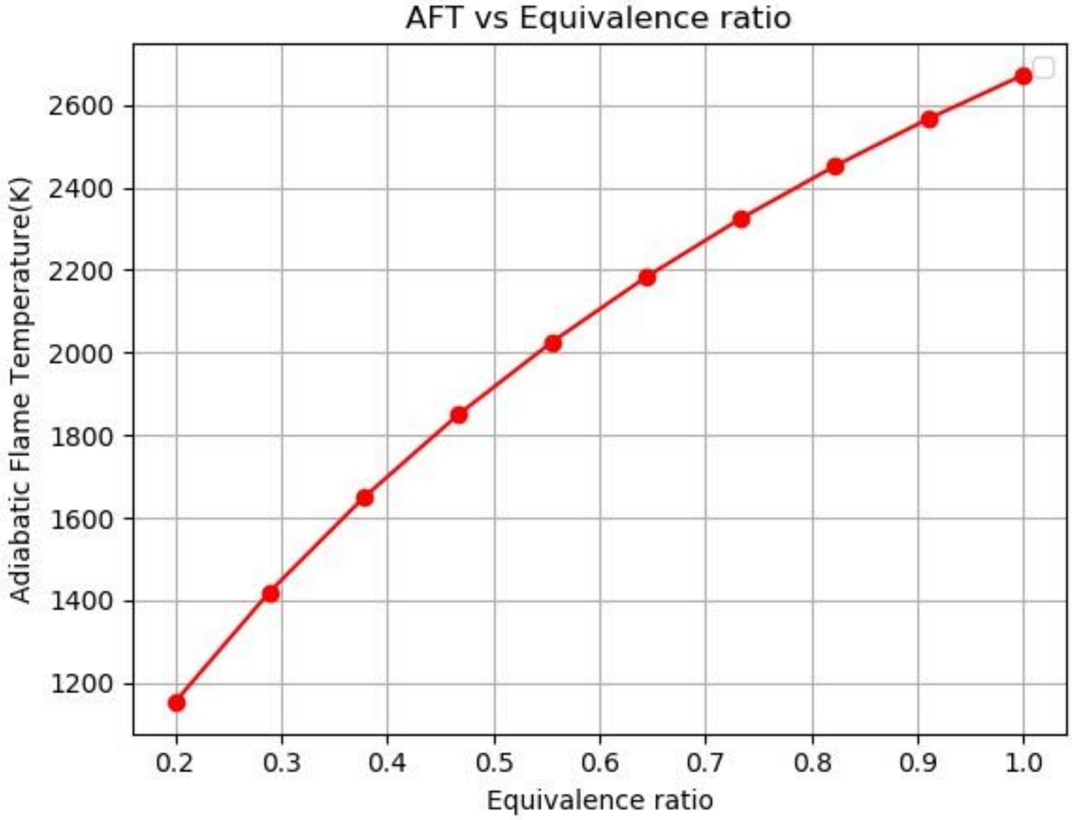


Figure 3.4: Effect of equivalence ratio on adiabatic flame temperature

From graph, at the equivalence ratio of 0.65, we get the adiabtic flame temperature of 2200 K approximately which is identical to the adiabatic flame temeprature of coal/air combustion as calculated in subchapter (3.4.1.2).

4 Design calculation results and discussion

The design calculations of the modified cement kiln system that implies calcination applying hydrogen combustion in oxygen in a carbon dioxide rich atmosphere to calcine the raw meal are performed in this chapter to determine an appropriate capacity of water electrolyzers for the production of hydrogen and oxygen fuel as per required for our specified system, constructional changes required for the existing calciner system depending on the parameters including velocity of gases in the calciner required for the particle to be fully entrained, recycle ratio of CO_2 back to calciner and reaction time of raw meal limestone particles.

4.1 The significant aspects in the design of new calciner system

According to the results of the measurement of gas velocity in the calciner to ensure full particle entrainment from sub-chapter (3.3.2), two significant aspects of the design of new calciner system were discovered with an options including tuning the CO_2 recycle ratio and constructional changes of a calciner with a smaller diameter than the diameter of current existing calciner i.e. (3.74 m).

However, the option of implying cnstructional changes of calciner will result in an increase in our total CAPEX value. While on the other hand, increasing the recycle ratio would also increase the amount of hydrogen fuel required for the new system, resulting in higher OPEX value. The design estimate of the constructional changes needed for the current existing calciner is shown in subchapter 4.1.1 in order to meet the needs of our new specified calciner system. The required capacity of the water electrolyzer is calculated in subchapter 4.1.2 based on the appropriate CO_2 recycle ratio determined for the system in subchapter 4.1.1.

4.1.1 Constructional changes required for the new calciner system

As discussed in subchapter 4.1 regarding the important aspects in the design of new calciner system, we are considering the choice of tuning the CO_2 recycle ratio as well as the change in diameter of the calciner for our defined system with a design calculation procedure and design basis values as shown in Figure 4.1 and Table 4.1 below.

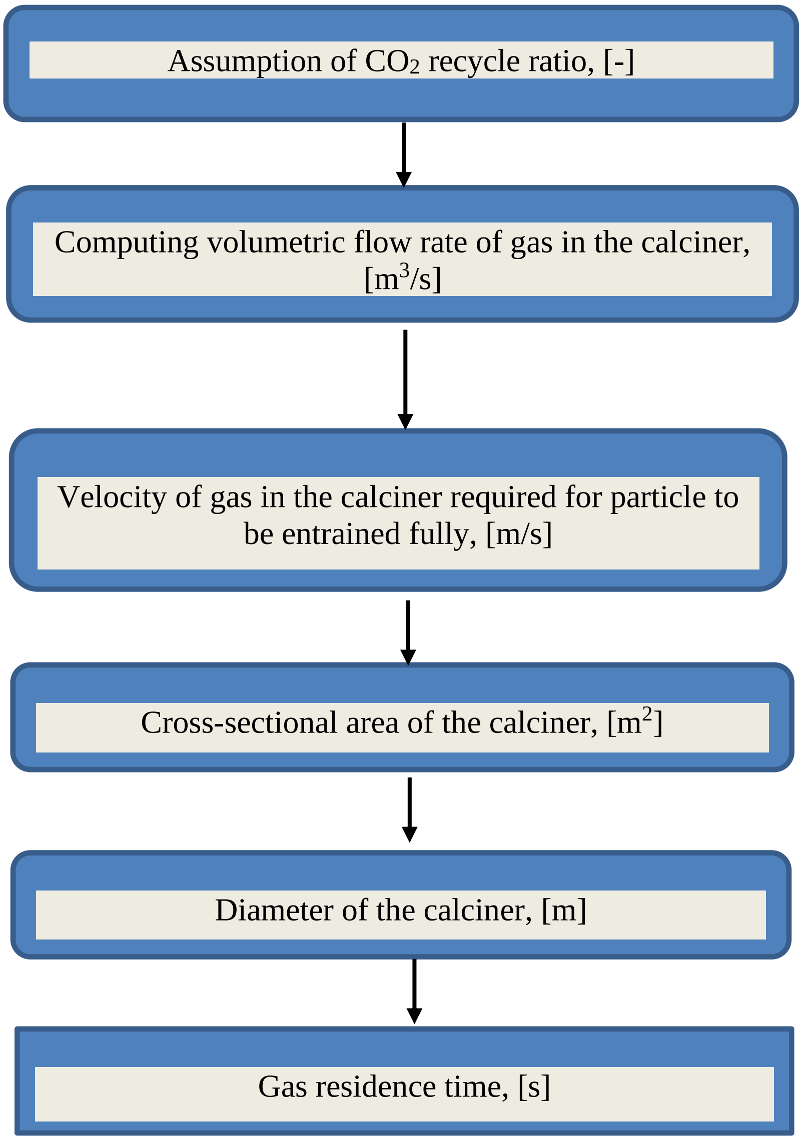


Figure 4.1: Design calculation procedure of new calciner system

Table 4.1: Design basis value for the new calciner system

Parameters	Value	Unit
Maximum size of raw meal particle, $d_{p,max}$	1000	[µm]
Height of calciner, H_{calc}	36.50	[m]
Lower limit of recycle ratio of CO_2	0.1	[-]
Range limit of gas residence time, $t_{gas,r}$	2-3	[s]

Following the procedure as summarized in Figure 4.1 to figure out the size and other important parameters for the design of our new calciner system.

1) Assumption of CO_2 recycle ratio:

The amount of hydrogen and oxygen fuel required for the system to calcine the raw meal is directly dependent on CO_2 recycle rate. Thus, to minimize the operational cost value for our new system, considering minimum recycle ratio i.e. $r_r = 0.1$ (assumption).

2) Calculating the volumetric flow rate of gas in the calciner:

As calculated in subchapter (3.3.2), volumetric flow rate of gas in the calciner with the CO_2 recycle ratio of 0.1 is

$$\dot{V}_{gas} = 46.97\ m^3/s$$

3) Velocity of gas required in the calciner to ensure particles to be fully entrained:

As calculated in subchapter (3.3.1), the terminal settling velocity of the raw meal particle of maximum size i.e. 1000 µm are: -

For CO_2 gas at T = 50°C , (V_t) = 6.06 m/s
For CO_2 gas at T = 900°C, (V_t) = 5.84 m/s
For H_2O gas at T = 900°C, (V_t) = 12.31 m/s

For the particle to be fully entrained, velocity of gas in the calciner must be greater than terminal settling velocity of the particles settling in a gas existing inside calciner. Thus, considering design basis value of the velocity of gas in the calciner to be: -

$$\text{Velocity of gas } (V_{gas}) = 12.5\ m/s$$

4) Calculating the cross-sectional area of the calciner:

$$\text{Cross-sectional area of calciner } (A_{cal}) = \frac{\text{volumetric flow rate } (\dot{V}_{gas})}{\text{Velocity of gas } (V_{gas})}$$

$$\therefore (A_{cal}) = \frac{46.97}{12.5} = 3.75\ m^2$$

5) Calculating diameter of the calciner:

$$\text{Diameter of calciner } (D_{cal}) = \sqrt{\frac{4 \cdot A_{cal}}{\pi}} = 2.18\ m$$

6) Gas Residence time:

The gas residence time $(t_{gas,r})$ can be calculated by using below equation (4.1).

$$t_{gas,r} = \frac{V_{cal}}{\dot{V}_{gas}} = \frac{A_{cal} \times H_{calc}}{\dot{V}_{gas}} \qquad 4.1$$

where,

V_{cal} = Volume of the calciner [m^3]

$\dot{V}_{gas}$ = Volumetric flow rate of gas in the calciner [m^3/s]

$\therefore t_{gas,r} = \frac{3.75 \times 36.50}{46.97} = 2.91\ s$ (acceptable in accordance to our design basis value, Table 4.1)

4.1.2 Design calculation consideration for no constructional modifications to the existing calciner

The main purpose of considering the new design calculation is to neglect the constructional changes required for the existing calciner system to reduce the capital expenditure for our new specified system. However, considering the only option of tuning CO_2 recycle ratio will increase operational expenditure to some extent which is estimated in chapter 6.

New design basis value is shown in Table 4.2 below.

Table 4.2: New design basis values

Parameters	Value	Unit
Maximum size of raw meal particle, $d_{p,max}$	500	[µm]
Diameter of the calciner, D_{cal}	3.74	[m]
Height of calciner, H_{calc}	36.50	[m]
Range limit of gas residence time, $t_{gas,r}$	2-3	[s]

With this new assumption, following the same procedure to design the calciner as summarized in Figure 4.1.

1. Assumption of CO_2 recycle ratio:

To ensure the raw meal particles to be fully entrained alone by tuning CO_2 recycle ratio and neglecting constructional changes to the existing calciner, we need to consider higher CO_2 recycle rate.

Therefore,
$r_r = 0.6$ (assumption)

2. Calculating the volumetric flow rate of gas in the calciner:

$\dot{V}_{gas} = 67.28\ m^3/s$ (refer to the calculation from subchapter 3.3.2 with a change of $r_r = 0.6$)

3. Velocity of gas required in the calciner to ensure particles to be fully entrained:

The terminal settling velocity of the raw meal particle of maximum size i.e. 500 µm is calculated as per the calculation example from subchapter (3.3.1): -
For CO_2 gas at T = 50°C , (V_t) = 2.82 m/s
For CO_2 gas at T = 900°C, (V_t) = 2.71 m/s

For H_2O gas at T = 900°C, (V_t) = 5.72 m/s

For the particle to be fully entrained, velocity of gas in the calciner must be greater than terminal settling velocity of the particles settling in a gas existing inside calciner. Thus, considering design basis value of the velocity of gas in the calciner,

Velocity of gas (V_{gas}) = 6 *m/s*

4. Calculating the cross-sectional area of the calciner:

$$A_{cal} = \frac{\pi {D_{cal}}^2}{4}$$

$$\therefore (A_{cal}) = \frac{\pi \times (3.74)^2}{4} = 10.98\ m^2$$

5. Calculating actual gas velocity in the calciner:

$$V_{gas} = \frac{\dot{V}_{gas}}{A_{cal}}$$

$$\therefore V_{gas} = \frac{67.28}{10.98} = 6.13\ m/s$$

The required gas velocity in the calciner as calculated in step 4 above is 6 m/s. Thus, the actual velocity of gas in the calciner is sufficient to ensure the particles to be fully entrained.

6. Gas Residence time:

$$t_{gas,r} = \frac{V_{cal}}{\dot{V}_{gas}} = \frac{A_{cal} \cdot H_{calc}}{\dot{V}_{gas}}$$

where,

V_{cal} = Volume of the calciner [m^3]

$\dot{V}_{gas}$ = Volumetric flow rate of gas in the calciner [m^3/s]

$$\therefore t_{gas,r} = \frac{10.98 \times 36.50}{67.28} = 5.95\ s$$

The calculated gas residence time based on the new design basis is long enough for the fuel to be completely burned in our specified new calciner system.

4.2 Design calculation of water electrolyzer

The design calculation of water electrolyzer is done based on the new design basis values with an assumption of CO_2 recycle ratio as 0.6. Figure 4.2 below depicts the design calculation procedure to determine the appropriate size and capacity of water electrolyzer required for our specified system.

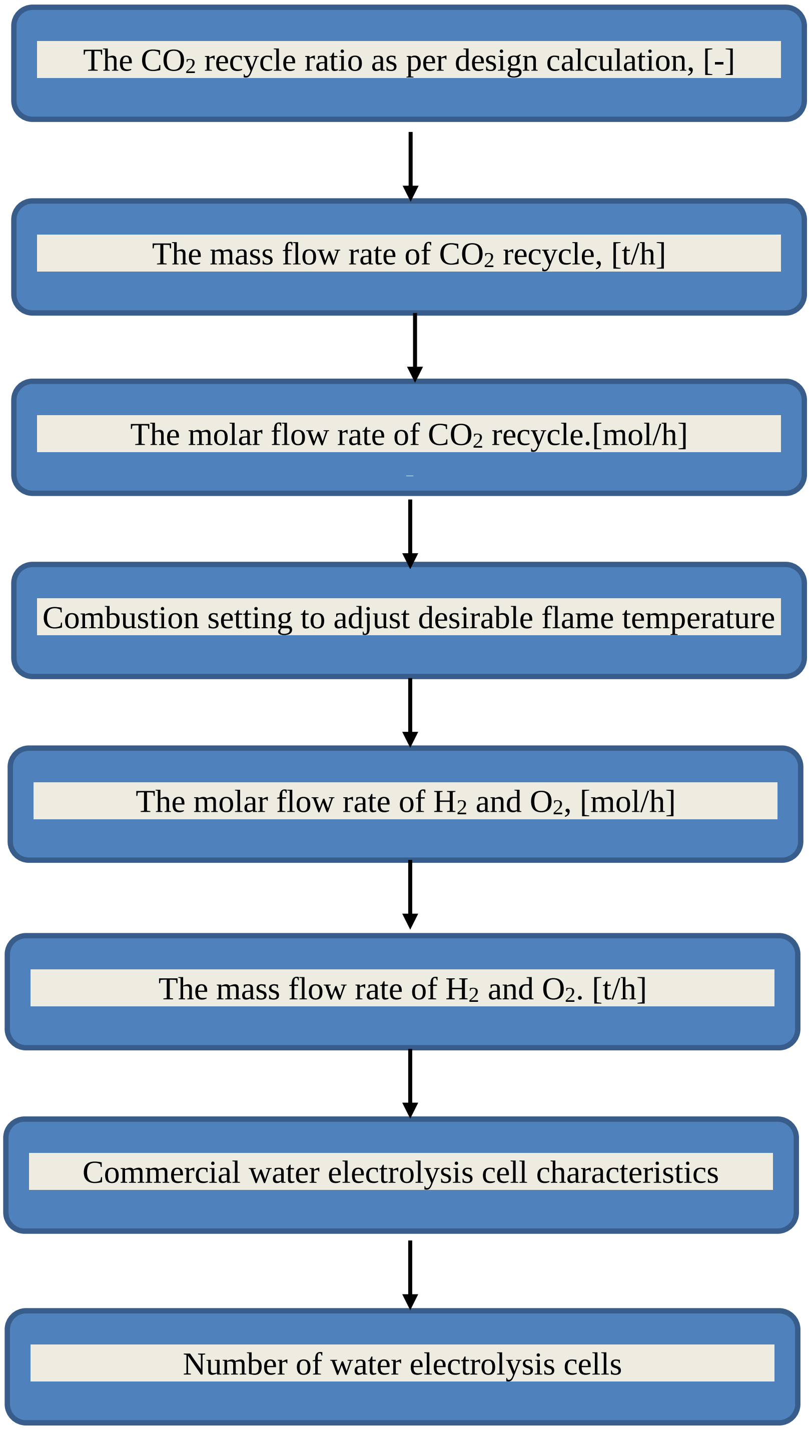


Figure 4.2: Design calculation procedure of water electrolyzer

Following the procedure outlined in Figure 4.2.

a. CO_2 recycle ratio, $r_r = 0.6$

b. Calculating the mass flow rate of CO_2 recycle:

To compute the mass flow rate of CO_2 recycled back to the calciner ($\dot{m}_{CO_2,r}$), equation 3.7 can be used.

$$\dot{m}_{CO_2,r} = r_r \cdot \dot{m}_{CO_2,m}$$

where,

$\dot{m}_{CO_2,m}$ = total CO_2 generated by meal in pre-calciner [t/h]

$$\therefore \dot{m}_{CO_2,r} = 0.6 \times 66.83 = 40.098 \left[\frac{t}{h}\right]$$

c. Calculating the molar flow rate of CO_2 recycle:

Molar flow rate of CO2 recycled back to the calciner ($\dot{n}_{CO_2,r}$) can be determined using equation 3.19.

$$\dot{n}_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{M_{CO_2}}$$

where,

$\dot{m}_{CO_2,r}$= mass flow rate of recycle CO_2 [t/h]

M_{CO_2}= molecular mass of CO_2 = 44.009× 10^{-3} [kg/mol]

$$\therefore \dot{n}_{CO_2,r} = \frac{40.098 \times 10^3}{44.009 \times 10^{-3}} = 911131.8 \left[\frac{mol}{h}\right]$$

d. Determining the appropriate combustion setting in the calciner to adjust desirable flame temperature:

From graph of Figure 3.3, at the equivalence ratio (∅) of 0.65, we get the adiabatic flame temperature of 2200 K approximately which is identical to the adiabatic flame temeprature of coal/air combustion as calculated in subchapter (3.4.1.2). As a result, the combustion reaction of our specified system, which involves hydrogen combustion in oxygen in a carbon dioxide-rich atmosphere to calcine the raw meal, is as follows: -

$$H_2 + 0.5O_2 + \frac{1}{\emptyset}CO_2 \rightarrow H_2O + \frac{1}{\emptyset}CO_2 + heat$$

$$H_2 + 0.5O_2 + 1.538CO_2 \rightarrow H_2O + 1.538CO_2 + heat$$

That means that for every one mole of hydrogen fuel and half mole of oxygen fuel to be combusted, (n=1.538 moles) of CO_2 are recycled back to the calciner.

e. Calculating the molar flow rate of H_2 and O_2 fuel required:

The molar flow rate of hydrogen ($\dot{n}_{H_2}$) and oxygen gas ($\dot{n}_{O_2}$) are calculated using equation (3.20) and (3.22).

$$\dot{n}_{H_2} = \frac{\dot{n}_{CO_2,r}}{n} = \frac{911131.8}{1.538} = 592413.4 \left[\frac{mol}{h}\right]$$

$$\dot{n}_{O_2} = \frac{n_{o_2}}{n} \cdot \dot{n}_{CO_2,r} = \frac{0.5}{1.538} \times 911131.8 = 296206.7 \left[\frac{mol}{h}\right]$$

f. Calculating the mass flow rate of H_2 and O_2 fuel required:

The mass flow rate of hydrogen ($\dot{m}_{H_2}$) and oxygen gas ($\dot{m}_{O_2}$) are calculated using equation (3.21) and (3.23).

$$\dot{m}_{H_2} = \dot{n}_{H_2} \cdot M_{H_2}$$

$$\dot{m}_{O_2} = \dot{n}_{O_2} \cdot M_{O_2}$$

where,

M_{H_2}= molecular mass of hydrogen = 2.016×10^{-3} [kg/mol]

M_{O_2}= molecular mass of oxygen =31.998×10^{-3} [kg/mol]

$$\therefore \dot{m}_{H_2} = 592413.4 \times 2.016 \times 10^{-3} = 1194.3 \left[\frac{kg}{h}\right] = 28.66 \left[\frac{ton}{day}\right]$$

$$\therefore \dot{m}_{O_2} = 296206.7 \times 31.998 \times 10^{-3} = 9478.02 \left[\frac{kg}{h}\right] = 227.47 \left[\frac{ton}{day}\right]$$

g. Commercial water electrolysis cell characteristics:

For the design consideration to our specified system, NEL ASA's atmospheric alkaline water electrolyzer model A3880 was chosen [31]. The atmospheric alkaline water electrolyzer characteristics is shown in Table 4.3 below and the Appendix G contains the various models and specifications of the water electrolysis cells.

Table 4.3: Specifications of water eletrolyzer of model A3880

Parameter	Value	Unit
Net production rate (0°C, 1 bar)	3880 8374	[Nm^3/h] [kg/day]
Power consumption	4.4	[kWh/Nm^3]
H_2 purity	99.999	[%]
O_2 purity	99.5	[%]
Area	770	[m^2]
Ambient temperature	5-35	[°C]

h. Required number of water electrolysis cells:

From specifications shown in table 4.3:

Production rate of hydrogen ($\dot{m}_{H_2,A3880}$) = 8374 kg/day

Hence, number of electrolysis cell (N_{ec}) needed for our system can be calculated using below equation 4.2.

$$N_{ec} = \frac{\dot{m}_{H_2}}{\dot{m}_{H_2,A3880}} \qquad 4.3$$

$$\therefore N_{ec} = \frac{28.86 \times 10^3}{8374} \sim 4$$

4.3 Design results and discussion

According to the results of the calciner design calculation in sub-chapter 4.1.1, the diameter of existing cement calciner must be modified, and the CO_2 recycle ratio must be kept at 0.5. This will lead to the increase in CAPEX and OPEX values for our specified system.

However, if we can ensure that the maximum size of raw meal limestone particles entering the calciner does not exceed 500 µm, we can ignore the constructional changes of the existing calciner and keep the CO_2 recycle ratio at 0.6, according to calculations in sub-chapter 4.1.2. The other relevant equipment units that must be installed for our modified cement kiln system are mentioned below:

- A water electrolyzer with calculated number of electrolysis cells and specified capacity must be installed.
- It is necessary to install storage tanks to store the excess hydrogen and oxygen fuel produced by water electrolyzer.
- A heat exchanger must be installed to utilize the excess heat from the gases exiting from calciner [32].
- To separate pure CO_2 gas from water vapor, a condenser must be placed.
- To recycle the CO_2 gas from the condenser back to the calciner, a CO_2 fan and gas ducts is necessary to be assembled.

5 Cost estimation theory

This section addresses the various cost analysis theories used for the estimation of cost in this thesis.

5.1 Capacity factor method

This approach can be used if the cost(A) and capacity(A) of an equipment are available and cost(B) estimation of the same equipment with different capacities(B) is needed and the respective equation is as (5.1) [24].

$$Cost\ of\ B = Cost\ of\ A\ \times (\frac{Capacity\ of\ A}{Capacity\ of\ B})^{e} \qquad 5.1$$

where,

exponent e = capacity factor for the facility whose value can vary in between 0.4 and 0.9 [33].

5.2 Detailed factor method

This method is used to calculate the total capital cost of all plant equipment's. Nils Henrik Eldrup of USN, Porsgrunn, created a table that includes direct cost, engineering cost, administration cost, and overall cost of various material types, sizes, and types of equipment as shown in Table 5.1.

For Carbon Steel (CS), Detailed Factor Table (DFT) is presented. If the material type of the equipment differs from carbon steel, the total installed cost factor in the table needs to be adjusted to determine the total installed cost factor for the desired material (f_{TIC}) as equation 5.2 below [32].

$$f_{TIC} = f_{TIC,CS} - f_{EQ,CS} + \left(f_{EQ,CS} \cdot m_f\right) - f_{PI,CS} + (f_{PI,CS} \cdot m_f) \qquad 5.2$$

where,

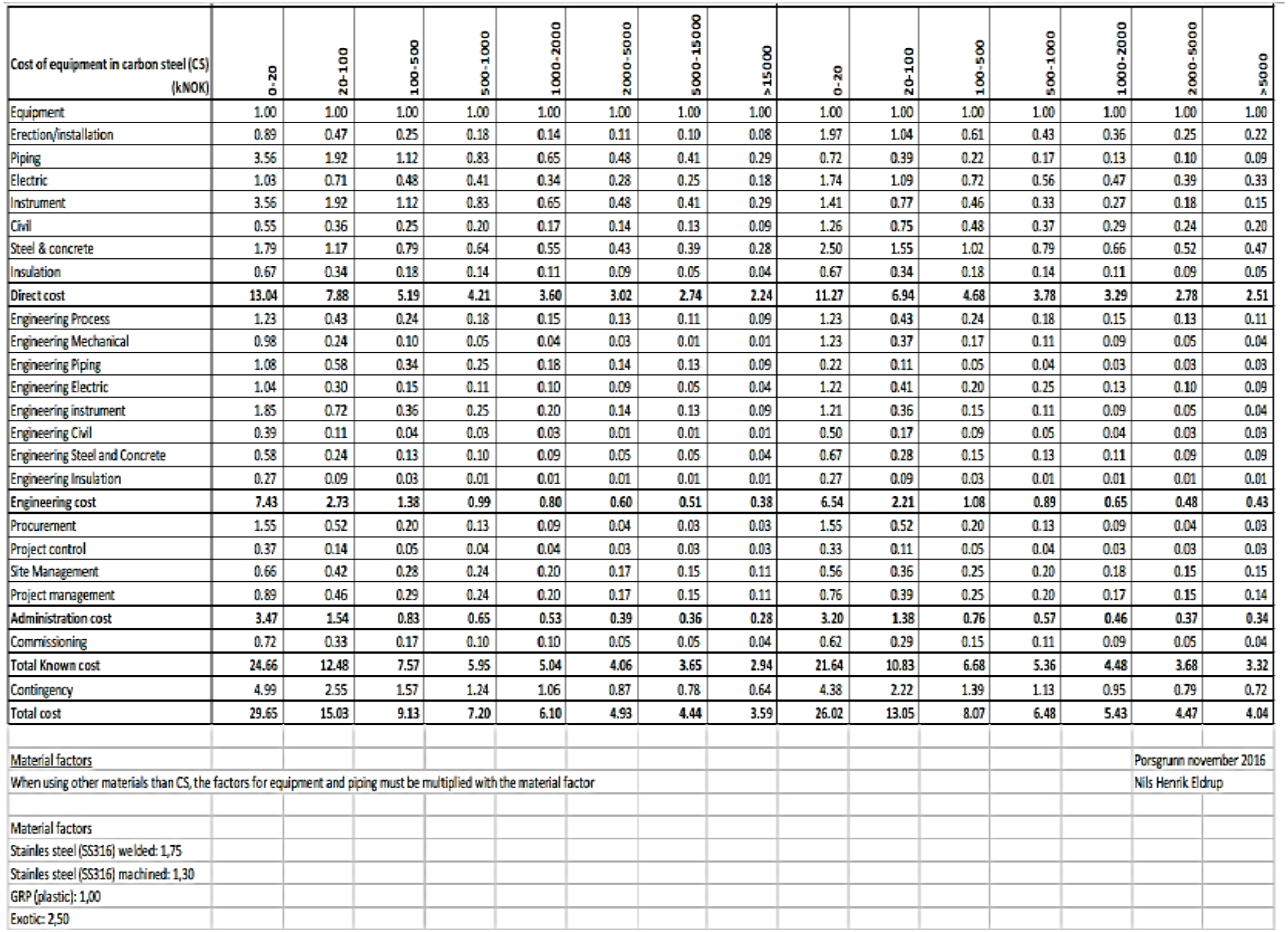
$f_{TIC,CS}$ = Total installed cost factor of CS material, [-]

$f_{EQ,CS}$ = cost factor for CS equipment from DFT, [-]

m_f = material factor, [-]

$f_{PI,CS}$ = cost factor for CS piping from DFT, [-]

Table 5.1: Detailed Factor Table (DFT)



Cost of equipment in carbon steel (CS) (kNOK)	0-20	20-100	100-500	500-1000	1000-2000	2000-5000	5000-15000	>15000	0-20	20-100	100-500	500-1000	1000-2000	2000-5000	>5000
Equipment	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Erection/installation	0.89	0.47	0.25	0.18	0.14	0.11	0.10	0.08	1.97	1.04	0.61	0.43	0.36	0.25	0.22
Piping	3.56	1.92	1.12	0.83	0.65	0.48	0.41	0.29	0.72	0.39	0.22	0.17	0.13	0.10	0.09
Electric	1.03	0.71	0.48	0.41	0.34	0.28	0.25	0.18	1.74	1.09	0.72	0.56	0.47	0.39	0.33
Instrument	3.56	1.92	1.12	0.83	0.65	0.48	0.41	0.29	1.41	0.77	0.46	0.33	0.27	0.18	0.15
Civil	0.55	0.36	0.25	0.20	0.17	0.14	0.13	0.09	1.26	0.75	0.48	0.37	0.29	0.24	0.20
Steel & concrete	1.79	1.17	0.79	0.64	0.55	0.43	0.39	0.28	2.50	1.55	1.02	0.79	0.66	0.52	0.47
Insulation	0.67	0.34	0.18	0.14	0.11	0.09	0.05	0.04	0.67	0.34	0.18	0.14	0.11	0.09	0.05
Direct cost	**13.04**	**7.88**	**5.19**	**4.21**	**3.60**	**3.02**	**2.74**	**2.24**	**11.27**	**6.94**	**4.68**	**3.78**	**3.29**	**2.78**	**2.51**
Engineering Process	1.23	0.43	0.24	0.18	0.15	0.13	0.11	0.09	1.23	0.43	0.24	0.18	0.15	0.13	0.11
Engineering Mechanical	0.98	0.24	0.10	0.05	0.04	0.03	0.01	0.01	1.23	0.37	0.17	0.11	0.09	0.05	0.04
Engineering Piping	1.08	0.58	0.34	0.25	0.18	0.14	0.13	0.09	0.22	0.11	0.05	0.04	0.03	0.03	0.03
Engineering Electric	1.04	0.30	0.15	0.11	0.10	0.09	0.05	0.04	1.22	0.41	0.20	0.25	0.13	0.10	0.09
Engineering instrument	1.85	0.72	0.36	0.25	0.20	0.14	0.13	0.09	1.21	0.36	0.15	0.11	0.09	0.05	0.04
Engineering Civil	0.39	0.11	0.04	0.03	0.03	0.01	0.01	0.01	0.50	0.17	0.09	0.05	0.04	0.03	0.03
Engineering Steel and Concrete	0.58	0.24	0.13	0.10	0.09	0.05	0.05	0.04	0.67	0.28	0.15	0.13	0.11	0.09	0.09
Engineering Insulation	0.27	0.09	0.03	0.01	0.01	0.01	0.01	0.01	0.27	0.09	0.03	0.01	0.01	0.01	0.01
Engineering cost	**7.43**	**2.73**	**1.38**	**0.99**	**0.80**	**0.60**	**0.51**	**0.38**	**6.54**	**2.21**	**1.08**	**0.89**	**0.65**	**0.48**	**0.43**
Procurement	1.55	0.52	0.20	0.13	0.09	0.04	0.03	0.03	1.55	0.52	0.20	0.13	0.09	0.04	0.03
Project control	0.37	0.14	0.05	0.04	0.04	0.03	0.03	0.03	0.33	0.11	0.05	0.04	0.03	0.03	0.03
Site Management	0.66	0.42	0.28	0.24	0.20	0.17	0.15	0.11	0.56	0.36	0.25	0.20	0.18	0.15	0.15
Project management	0.89	0.46	0.29	0.24	0.20	0.17	0.15	0.11	0.76	0.39	0.25	0.20	0.17	0.15	0.14
Administration cost	**3.47**	**1.54**	**0.83**	**0.65**	**0.53**	**0.39**	**0.36**	**0.28**	**3.20**	**1.38**	**0.76**	**0.57**	**0.46**	**0.37**	**0.34**
Commissioning	0.72	0.33	0.17	0.10	0.10	0.05	0.05	0.04	0.62	0.29	0.15	0.11	0.09	0.05	0.04
Total Known cost	**24.66**	**12.48**	**7.57**	**5.95**	**5.04**	**4.06**	**3.65**	**2.94**	**21.64**	**10.83**	**6.68**	**5.36**	**4.48**	**3.68**	**3.32**
Contingency	4.99	2.55	1.57	1.24	1.06	0.87	0.78	0.64	4.38	2.22	1.39	1.13	0.95	0.79	0.72
Total cost	**29.65**	**15.03**	**9.13**	**7.20**	**6.10**	**4.93**	**4.44**	**3.59**	**26.02**	**13.05**	**8.07**	**6.48**	**5.43**	**4.47**	**4.04**

Material factors

When using other materials than CS, the factors for equipment and piping must be multiplied with the material factor

Porsgrunn november 2016
Nils Henrik Eldrup

Material factors
Stainles steel (SS316) welded: 1,75
Stainles steel (SS316) machined: 1,30
GRP (plastic): 1,00
Exotic: 2,50

5.3 Cost adjustment for time (inflation/escalation)

Using the relevant cost indexes, the current cost of a facility can be calculated as equation (5.3) [33].

$$Present\ cost = Original\ cost \times \left(\frac{Index\ value\ at\ present}{Index\ value\ at\ time\ of\ original\ cost\ was\ obtained}\right) \qquad 5.3$$

5.4 Net present value (NPV)

The value of money varies over period depending on the interest rate. Money today is worth more than it would be in the future. The value of the future money decreases as interest rises. Future money can be defined as non-discounted cash flow if interest is not considered.

The current worth of non-discounted cash flow is given by Net Present Value (NPV) [32]. If a cash flow exists from year “n=0” to year “n=end”, then the NPV of the cash flow can be calculated using equation (5.4) [33].

$$NPV = \sum_{n=0}^{n=end} F_N \frac{1}{(1+i)^n}$$

NPV is the net present value (discounted cash flow), F_N is future value non-discounted cash flow, i is the interest rate and n is the number of timer periods.

5.5 Equivalent annual cost (EAC)

The annual cost of owing, operating, and maintaining the asset over its entire service life is known as equivalent annual cost (EAC). It is calculated by dividing the NPV by the annuity factor, as shown in equation (5.5).

$$EAC = \frac{NPV}{a_f} \qquad 5.5$$

where, a_f is the annuity factor and can be calculated using below equation (5.6).

$$a_f = \frac{1-\frac{1}{(1+i)^n}}{i} \qquad 5.6$$

Equation (5.7) and (5.8) can be applied to estimate the capital expenditure (CAPEX) and operational expenditure (OPEX) for each year.

$$EAC_{CAPEX} = \frac{NPV_{CAPEX}}{a_f} \qquad 5.7$$

$$EAC_{OPEX} = \frac{NPV_{OPEX}}{a_f} \qquad 5.8$$

Here,

NPV_{CAPEX} is the net present value of capital expenditure that comprises total installed cost of all equipment and NPV_{OPEX} is the net present value of operational expenditure [24].

6 Cost Estimation calculation

The cost estimation calculation of equipment units involved in our modified cement calciner system, which includes a water electrolyzer and a CO_2 fan, is presented in this chapter.

6.1 Basis of Calculation

The cost estimation of water electrolyzer and a CO_2 fan is calculated based on the design parameters of measured in chapter 4 which is then compared to the cost of purchasing electrical energy to estimate the net present value and equivalent annual cost.

6.1.1 Cost of Electricity

Table 6.1 below depicts the electricity price in Norway [34].

Electricity prices in the end-user market, quarterly. Øre/kWh

	1st quarter 2021	Change in per cent	
	Øre/KwH	Last 3 mos.	Last 12 mos.
Households. Total price of electricity, grid rent and taxes	120.0	45.6	36.7
Electricity price	53.5	141.0	99.6
Grid rent	27.6	-3.5	-4.5
Taxes	38.9	23.1	21.2
Households. Electricity price by type of contract. Exclusive taxes			
New fixed-price contracts-1 year or less [1]	32.3	32.9	-9.5
New fixed-price contracts-1 year or more [1]	32.4	0.3	-4.4
All other fixed-price contracts	36.6	8.6	-4.4
Contracts tied to spot price	53.8	166.3	134.9
Variable price (not tied to spot price)	54.4	90.9	35.0
Business activity. Electricity price. Exclusive taxes			
Services	49.1	168.3	99.6
Manufacturing excl. energy-intensive manufacturing	49.4	180.7	116.7
ManufacturiEnergy-intensive manufacturing	33.5	18.4	11.3

[1] New fixed-price contracts are entered during the measuring period, and older fixed-price contracts are entered earlier.

Figure 6.1: Electricity price in Norway [34]

Since the manufacturing of cement is highly energy intensive, the cost of electricity (C_{el}) is taken as 0.335 NOK/kWh as per Table 6.1.

6.1.2 Selection of water electrolyzer and CO_2 fan

Based on the required amount of hydrogen and oxygen fuel calculated in sub-chapter 4.2, i.e. 28.66 tons/day and 227.47 tons/day, an Alkaline water electrolysis cell of model A3880 that can produce 8374 kg of hydrogen in a day, was chosen for this project. The characteristics of the respective electrolysis cell model is presented in Table 4.3.

A centrifugal radial fan with the benefits mentioned below has been considered in our specified system to recycle necessary amount of CO_2 back to the calciner [24].

- High pressure and medium flow
- Can withstand dust, moisture, and heat, making it ideal for industrial applications.

6.1.3 The recycling rate of CO_2

With the recycling ratio (r_r =0.6) as our design basis value for the new calciner system as calculated in sub-chapter 4.2.1, the mass flow rate of CO_2 recycling required was $\dot{m}_{CO_2,r} = 40.098 \text{ t/h}$.

Thus, the volumetric capacity required for the centrifugal radial fan to recycle the desired amount of CO_2 back to calciner can be calculated using equation (6.1).

$$Q_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{\rho_{CO_2}} \qquad 6.1$$

$$\therefore Q_{CO_2,r} = \frac{40.098}{0.4515} \times \left(\frac{1000}{3600}\right) = 24.67\ m^3/s$$

The price of centrifugal radial fan based on the volumetric capacity for CO_2 recycling is 16356 USD [35].

6.2 Total Installation cost for water electrolyzer

The capital investment cost of water electrolyzer system as per the U.S. Department of Energy (DOE) is 430 USD/kW in 2011 [36].

Based on the chosen model of water electrolysis cell that can produce 8374 kg of hydrogen in a day and number of water electrolysis cell needed for our system as calculated in sub-chapter (4.2), calculating the total installation cost of water electrolyzer as follows: -

Net production rate of hydrogen ($\dot{P}_{H_2}$)= 3880 Nm^3/h

Power consumption (ε_c)= 4.4 kWh/Nm^3

Number of electrolysis cell (N_{ec}) = 4

Total electrical power required for water electrolyzer can be calculated using equation (6.2).

$$\varepsilon_{el,we} = N_{ec} \cdot \dot{P}_{H_2} \cdot \varepsilon_c \qquad 6.2$$

$$\therefore \varepsilon_{el,we} = 4 \times 3880 \times 4.4 = 68288\ kW = 68.288\ MW$$

Therefore, the total installation cost of water electrolyzer is ($430 \times 68288 =$ 29.36 MUSD).

6.3 Cost adjustment based on currency

The currency exchange rate from USD to NOK is 8.25 [37]. Table 6.2 below depicts the total installation cost of equipment based on the currency conversion.

Table 6.2: Currency conversion

Equipment	Model	Capacity	Unit	Year	Currency	Cost
Water Electrolyzer	A3880	3880, N_{ec}=4	Nm^3/h	2011	MNOK	242.25
Centrifugal radial fan	--------	24.47	m^3/s	2002	kNOK	134.93

6.4 Cost adjustment based on inflation

The cost-index ratio between 2021 & 2011 and 2021 & 2002 for the cost adjustment of water electrolzer and centrifugal radial fan can be calculated using the inflation data shown in table 6.3 and 6.4 respectively.

Table 6.3: Inflation from 2002 to 2021 [38]

Year	USD value
2002	\$100
2021	\$148.45

Cost-index value in 2002 (C_{2002}) = \$100

Cost-index value in 2021 (C_{2021}) = \$148.45

Therefore,

Cost-index ratio between 2021 and 2002 is,

$$r_{CI,f} = \frac{C_{2021}}{C_{2002}} = 1.484$$

Table 6.4: Inflation from 2011 to 2021 [38]

Year	USD value
2011	\$100
2021	\$118.72

Cost-index value in 2011 (C_{2011}) = $100

Cost-index value in 2021 (C_{2021}) = $118.72

Therefore,

Cost-index ratio between 2021 and 2011 is,

$$r_{CI,f} = \frac{C_{2021}}{C_{2011}} = 1.187$$

Updating the table 6.2 for the installation cost of equipment as shown in Table 6.5.

Table 6.5: Updated installation cost of equipment [38]

Equipment	Model	Capacity	Unit	Year	Currency	Cost
Water Electrolyzer	A3880	3880, N_{ec}=4	Nm^3/h	2021	MNOK	287.55
Centrifugal radial fan	--------	24.47	m^3/s	2021	kNOK	200.23
Total installation cost	------	------	-----	2021	MNOK	287.75

6.5 Equivalent electricity cost calculation

The cost calculation input data is shown in Table 6.6 below [3].

Table 6.6: Cost input data

Parameter	Value	Unit
Operating hours	7315	[h/y]
Interest	7.5	[%]

The cost of electricity as per table 6.1, $C_{el,kWh} = 0.335$ NOK/kWh

Total electrical power required for water electrolyzer, $\varepsilon_{el,we} = 68288\ kW$

Hence, cost of equivalent electricity per year ($C_{el,yr}$) can be calculated using equation (6.3).

$$C_{el,yr} = C_{el,kWh} \cdot \varepsilon_{el,we} \cdot n_{h,yr} \tag{6.3}$$

where, $n_{h,yr}$ is the operating hours (refer to table 6.6).

$$\therefore C_{el,yr} = 0.335 \times 68288 \times 7315 = 167.34\ MNOK/year$$

6.6 Net present value calculation

According to cost estimation basis value (refer to table 6.6), rate of interest (i) = 7.5%

Assumption, number of years to buy electricity (n) = 15

Net present value can then be calculated using equation (5.4).

$$NPV = C_{el,yr} + \frac{C_{el,yr}}{(1+i)^1} + \frac{C_{el,yr}}{(1+i)^2} + \cdots + \frac{C_{el,yr}}{(1+i)^{n-1}}$$

$$= 1587.89\ MNOK/year$$

6.7 Equivalent annual cost calculation

Applying equation (5.6), to calculate the annuity factor, we get

$$a_f = \frac{1 - \frac{1}{(1+i)^n}}{i} = 8.49$$

Now, Determining the equivalent annual cost for capital expenditure and operational expenditure using equations (5.7) and (5.8).

$$EAC_{CAPEX} = \frac{NPV_{CAPEX}}{a_f} = \frac{287.75}{8.49} = 33.98\ MNOK/year$$

$$EAC_{OPEX} = \frac{NPV_{OPEX}}{a_f} = \frac{1587.89}{8.49} = 187.03\ MNOK/year$$

6.8 Cost per capture CO_2 unit

The only partial capture case of CO_2 from pre-calcination is considered since the CO_2 from the rotary kiln is not taken into account.

Design basis value (refer to sub-chapter 4.2)

Recycle ratio (r_r) = 0.6

Total amount of CO_2 avoided = $\dot{m}_{CO_2,m} - (r_r \times \dot{m}_{CO_2,m}) = 26.73$ [t/h]

Operation hour = 7315 [h/y]

$$\therefore \dot{m}_{CO_2,year} = 26.73 \times 7315 = 195529.95 \left[\frac{t}{y}\right]$$

Cost per captured CO_2 unit can be calculated using below equation (6.4) and (6.5).

$$CAPEX = \frac{\mathrm{EAC_{CAPEX}}}{\dot{m}_{CO_2,year}} = 173.8\ \frac{NOK}{tCO_2\ captured}$$

$$OPEX = \frac{\mathrm{EAC}_{OPEX}}{\dot{m}_{CO_2,year}} = 956.5\,\frac{NOK}{tCO_2\ captured}$$

Hence, the total cost per mass of CO2 captured is 1130.3$\frac{NOK}{tCO_2\ captured}$.

7 Conclusion

This current master's thesis investigated calcination applying H_2 combustion in O_2 in a CO_2 rich atmosphere to calcine the raw meal. The key design parameters such as terminal settling velocity, gas velocity in the calciner and adiabatic flame temperature were calculated. Three major water electrolysis technologies were studied as a part of literature study that included Alkaline water electrolysis, Polymer exchange membrane water electrolysis and Solid oxide water electrolysis.

The adiabatic flame temperature as a result of coal/air combustion in the existing calciner system and H_2 combustion in O_2 and CO_2 was investigated, and it was found that in order to maintain the same flame temperature in our modified calciner system, 1.538 moles of CO_2 recycling was needed for every one mole of H_2 and 0.5 mole of O_2 combustion. AFT resulted in a very high flame temperature (refer to Appendix I) as a result of H_2 combustion in O_2 neglecting the recycle of CO_2, which was concluded as the major reason for the need for CO_2 recycling to lower the flame temperature inside the calciner.

Terminal settling velocity of maximum size of raw meal limestone particles settling in a various gas present in the calciner were determined. The maximum particle size of 1000 μm was chosen as our design basis value, considering the phenomenon of lumping and clustering of the particles during the calcination process.

The two significant aspects for the design of new calciner system were discovered to ensure that the particles in the calciner are fully entrained. First option was to adjust the CO_2 recycle ratio to it's lower limit i.e. 0.1 and modifying the calciner with smaller diamter than the diameter of current existing calciner i.e. (3.74 m). The second option was the tuning of the CO_2 recycle ratio appropriate for our specified system without considering any constructional changes to the existing calciner.

The design diameter of calciner, 2.18m was found to be adequate to ensure full particle entrainment considering the first option of adjusting the CO_2 recycle ratio to its lower limit. The second option design consideration was determined on the assumption that the maximum particle size in the calciner would not exceed $500\mu m$ with the possibility of eliminating or reducing clustering and lumping phenomena inside calciner in a near future. Tuning the recycle ratio based on this design consideration, it was found out that with the recycle ratio of 0.6, all the particles in the calciner are fully entrained without requiring any modifications to the existing calciner. With the recycle ratio of 0.1 and 0.6, the required amount of hydrogen and oxygen fuel were determined and the total electrical power consumption by the water electrolyzer to produce the desired amount of fuels were found to be 18.409 MW and 68.288 MW, respectively.

For contrast, cost estimates were carried out for both design options with recycle ratios of 0.1 and 0.6. With a CO_2 recycle ratio of 0.1 and 0.6, the capital cost for the water electrolyzer and CO_2 fan was found to be 77.576 MNOK and 287.75 MNOK, respectively. And the cost per mass of CO_2 avoided was found to be 135.37 and 1130.3 NOK per ton of CO_2 avoided.

Based on a cost analysis of two design alternatives for the project's economic viability and sustainability, the first option, adjusting the CO_2 recycle ratio to it's lower limit of 0.1 and modifying the calciner with a diameter of 2.18m, appeared to be feasible. However, in the future, when water electrolyzers are designed with full output potential (Efficiency $\approx$ 99.99 %) and the electrolysis cell are powered by green electricity, the second design option would be the topic of interest.

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Appendices

Appendix A: Task description
Appendix B: Work Breakdown Structure (WBS)
Appendix C: MATLAB code to calculate mass and energy balance equations
Appendix D: Thermodynamics physical property table
Appendix E: Python code to calculate adiabatic flame temperature
Appendix F: NASA polynomials
Appendix G: Models and specifications of atmospheric alkaline water electrolyzers
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Appendix A: Task description

FMH606 Master's Thesis

Title: Calcination applying H_2 combustion in O_2 in a CO_2 rich atmosphere

USN supervisors: Lars-André Tokheim

External partners: Norcem AS Brevik

Task background:
USN is one of the partners in the research project *"Combined calcination and CO_2 capture in cement clinker production by use of CO_2-neutral electrical energy"*. The acronym ELSE[1] is used as a short name for the project. Phase 1 of the project was completed in April 2019, and Phase 2 was started in April 2020. The goal of the ELSE project is to utilize electricity (instead of carbon-containing fuels) to decarbonate the raw meal in the cement kiln process while at the same time capturing the CO_2 from decarbonation of the calcium carbonate in the calciner. A regular kiln system is shown in Figure 1.

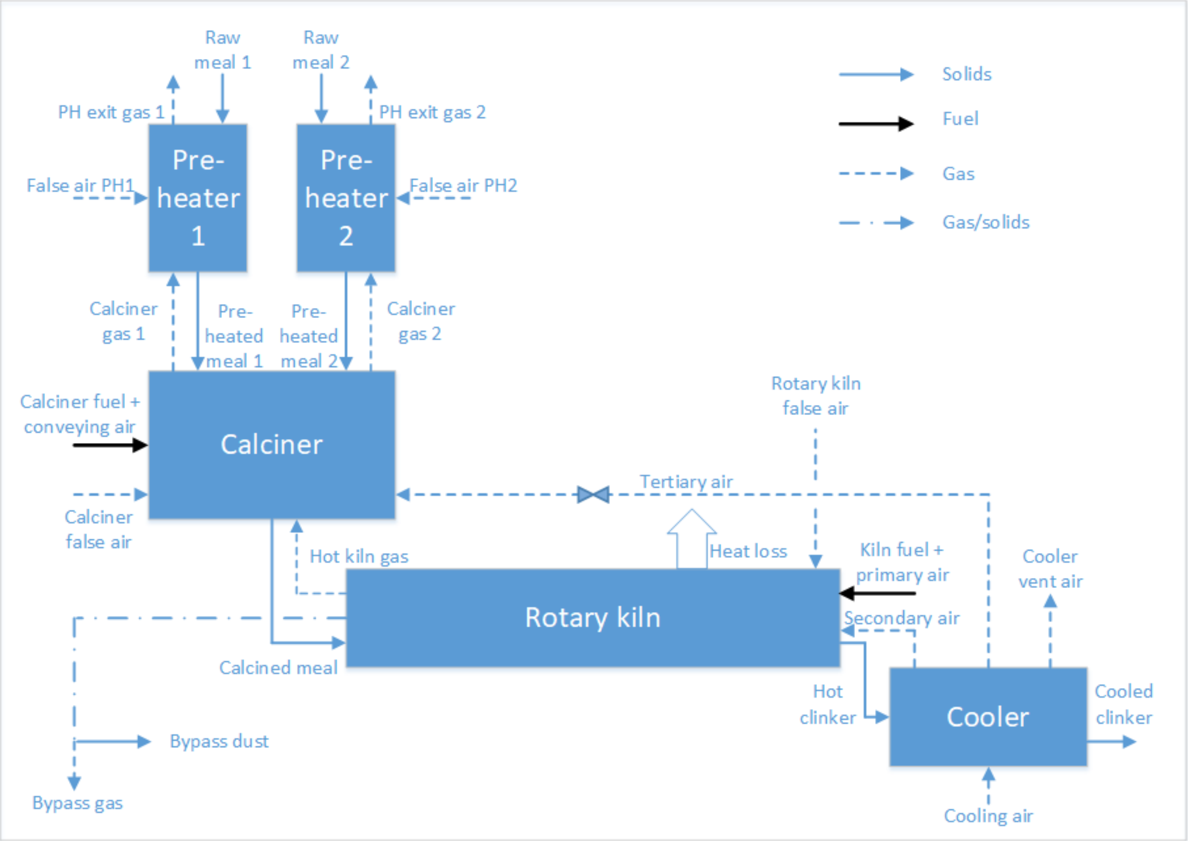

Figure 1: A regular cement kiln process with two preheater strings.

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[1] ELSE is short for '<u>EL</u>ektrifisert <u>SE</u>mentproduksjon' (Norwegian) meaning 'electrified cement production'.

Different concepts to implement electrification of the calciner have been discussed. One alternative is to use electricity to produce hydrogen in oxygen from water in an electrolysis process, and thereafter burn the hydrogen in oxygen in the calciner. An advantage of this is that the existing calciner may be used, maybe without doing big changes to the geometry etc.

If the hot kiln gas, the tertiary air and the carbon-containing fuels are no longer supplied to the calciner, then N_2 can be eliminated from the calciner exit gas, which will be a mixture of mainly CO_2 and H_2O. After condensation of the H_2O, the product will be more or less pure CO_2 (depending on the excess O_2 in the combustion reaction), which can be stored (or utilized in some way). Some recycling of CO_2 (or CO_2+H_2O) in the calciner is probably necessary to control the temperature and the combustion properties. A block-diagram illustrating a potential concept is given in Figure 2.

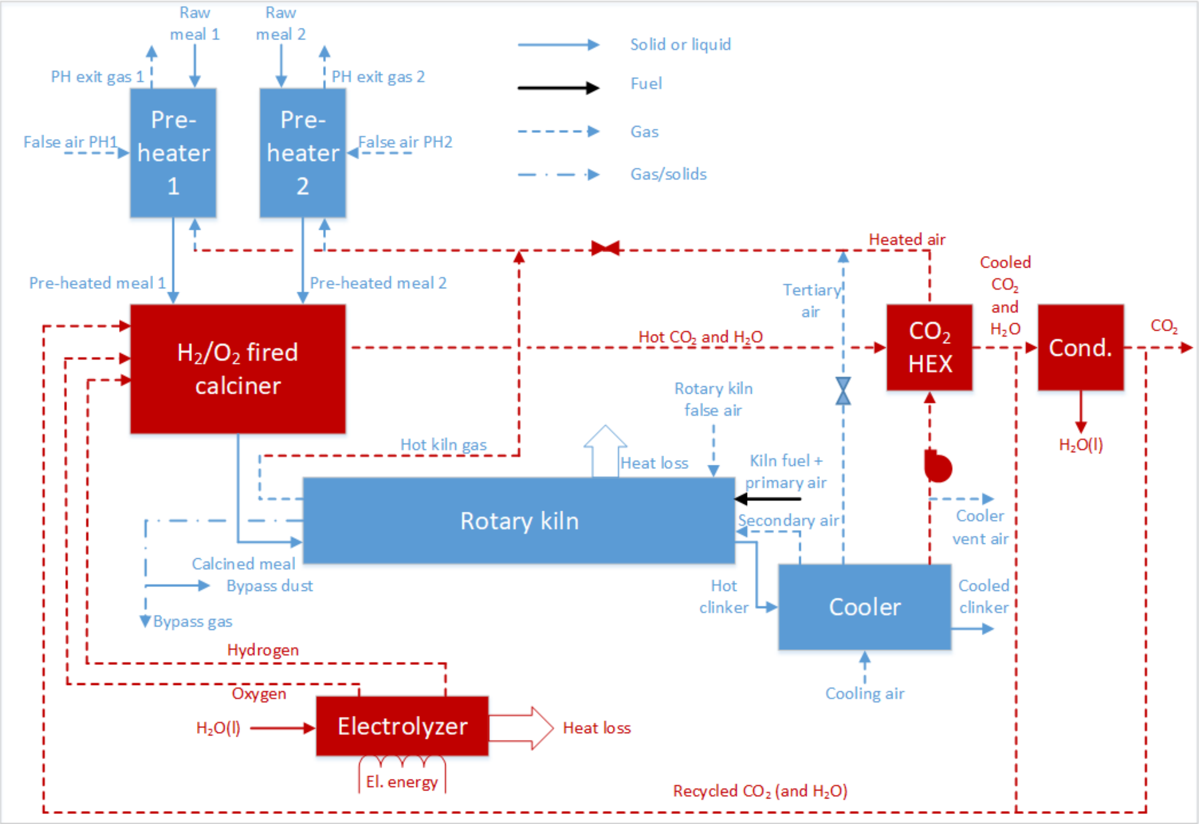


Figure 2: A modified cement kiln process applying hydrogen combustion for calcination.

Such a concept may be less expensive than a regular post-combustion system applied to CO_2 capture from the cement plant. Moreover, as the fuel generated CO_2 will be eliminated, less CO_2 is produced in the calcination process.

<u>Task description</u>:

The task may include the following:

- Make a literature study of the state of the art of water electrolysis for production of hydrogen and oxygen, explaining different technologies and addressing the energy losses in the electrolysis process
- Describe a process concept that combines electrolysis generated H_2 and O_2 with calcination based on combustion of H_2 in O_2 (with CO_2 recycling)
- Investigate how flame properties are affected by mixing H_2 and CO_2 (or CO_2+H_2O)
- Assess safety aspects related to production, handling and combustion of hydrogen and oxygen in a cement kiln environment
- Calculate adiabatic flame temperature as a function of CO_2 (or CO_2+H_2O) reycling rate
- Recommend a recycling rate for CO_2 (or CO_2+H_2O), taking into account the H_2O condenser downstream of the calciner
- Identify and quantify waste heat streams in the new system
- Evaluate potential usage of waste heat streams to increase the energy efficiency, either internally in the process or externally to for example district heating.
- Make a mass and energy balance of the system and calculate mass flow rates, temperatures, duties, etc.
- Make a process simulation model of (part of) the system and simulate different cases, varying key parameters in the system
- Make a process flow diagram with process values for selected cases
- Evaluate to what extent constructional changes to the existing calciner are required
- Determine the required size of the electrolyzer, the calciner, the condenser, the CO_2 fan, the gas ducts and possibly other relevant equipment units
- Make estimates of investment costs (CAPEX) and operational costs (OPEX) of the suggested process, including calculation of costs per avoided CO_2 unit (€/t_{CO2}).

Student category: EET or PT students

Is the task suitable for online students (not present at the campus)? Yes, both online and campus students may select the task.

Practical arrangements:

There may be meetings with Norcem to discuss the task and the progress, most likely via Skype/Teams/Zoom (due to the corona situation).

Supervision:

As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

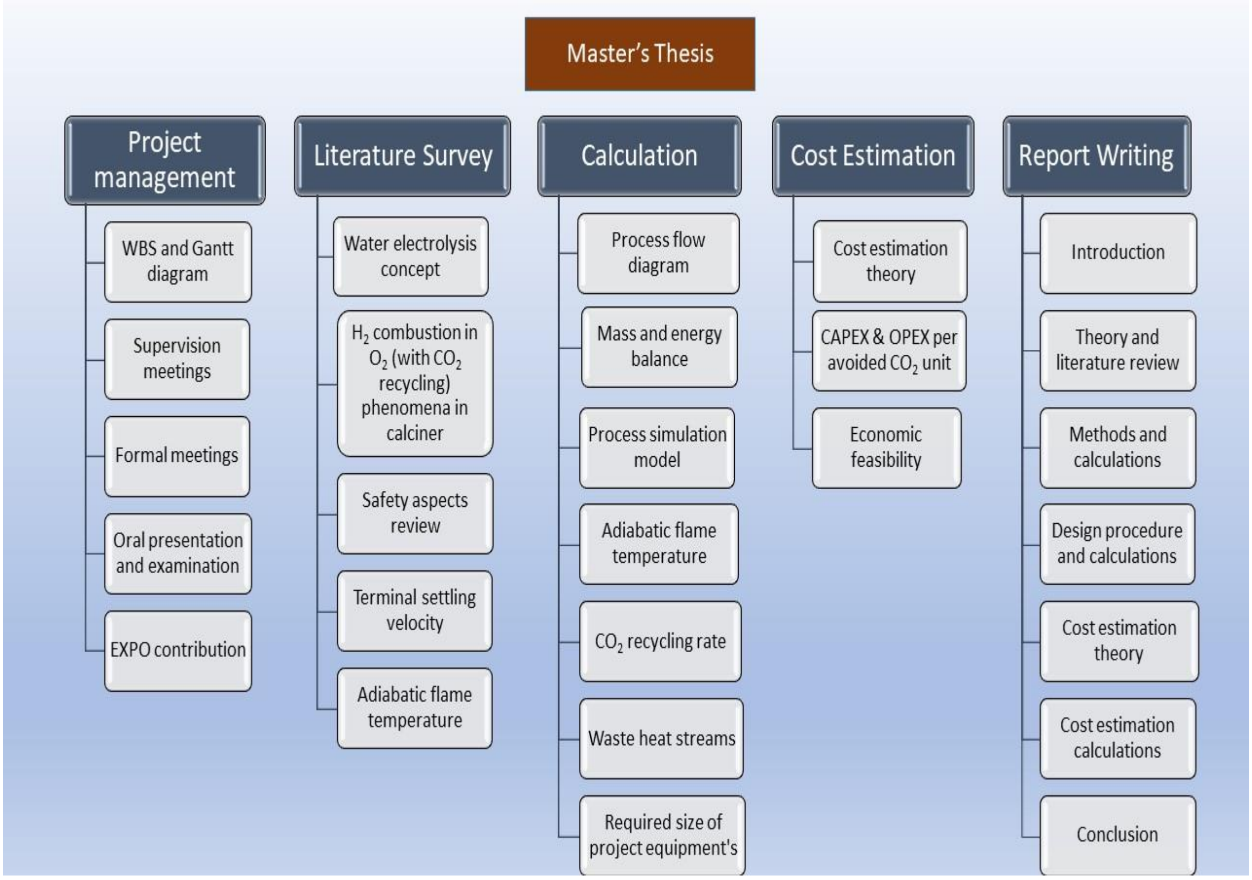
Signatures:

Supervisor (date and signature): 28.01.2021, Lars André Tokheim

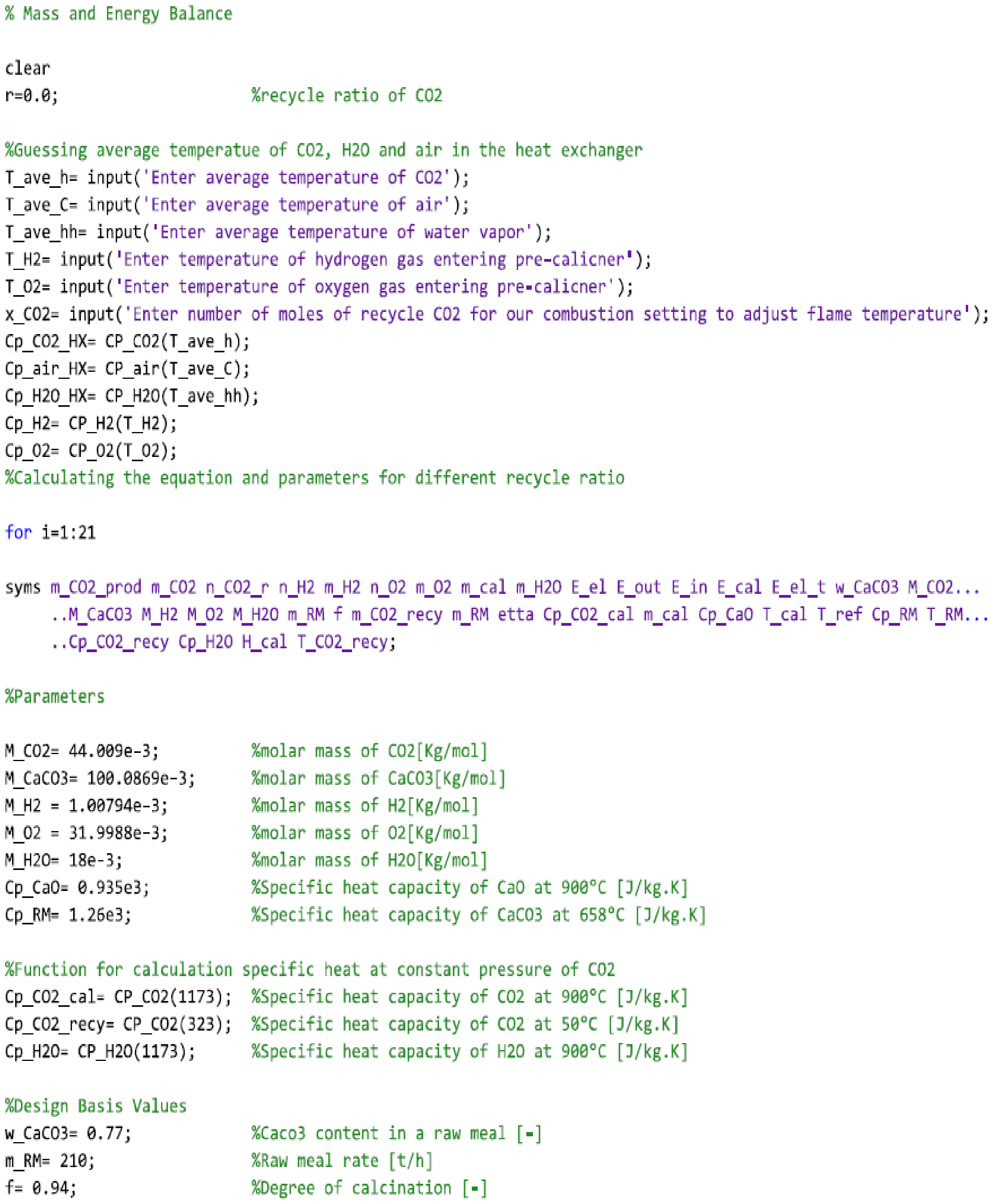
Student (write clearly in all capitalized letters): DIPENDRA KHADKA

Student (date and signature): 28.01.2021, Dipendra

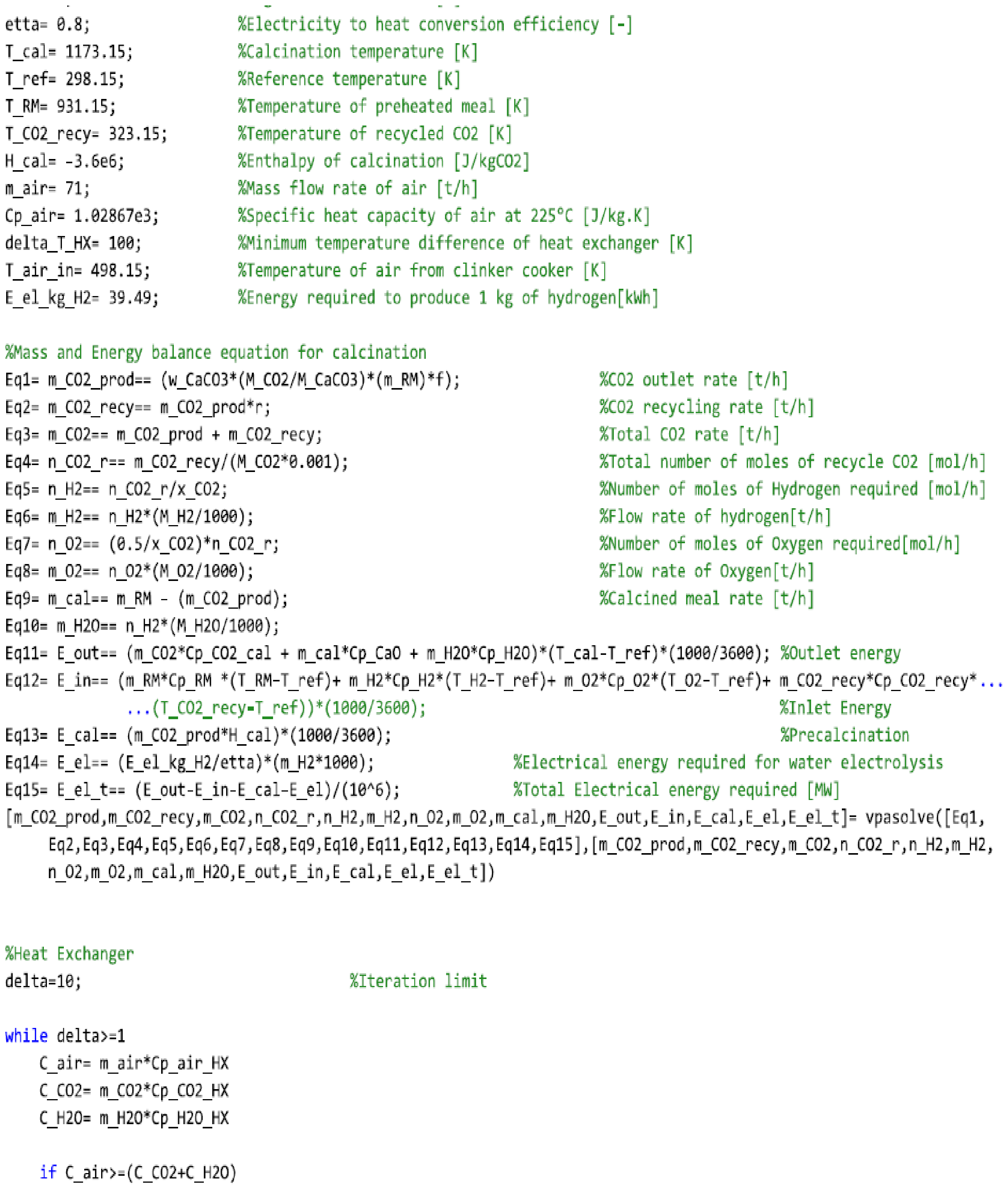
Appendix B: Work Breakdown Structure



Appendix C: MATLAB code to calculate mass and energy balance equations

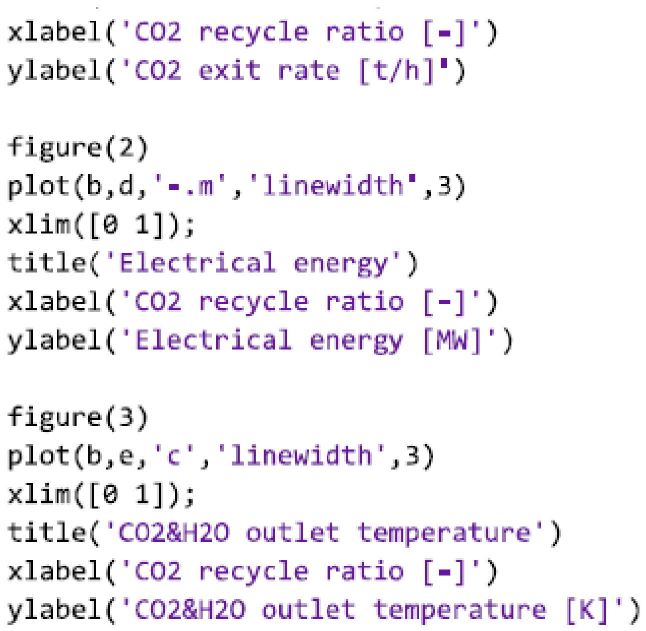


```
% Mass and Energy Balance

clear
r=0.0;                     %recycle ratio of CO2

%Guessing average temperatue of CO2, H2O and air in the heat exchanger
T_ave_h= input('Enter average temperature of CO2');
T_ave_C= input('Enter average temperature of air');
T_ave_hh= input('Enter average temperature of water vapor');
T_H2= input('Enter temperature of hydrogen gas entering pre-calicner');
T_O2= input('Enter temperature of oxygen gas entering pre-calicner');
x_CO2= input('Enter number of moles of recycle CO2 for our combustion setting to adjust flame temperature');
Cp_CO2_HX= CP_CO2(T_ave_h);
Cp_air_HX= CP_air(T_ave_C);
Cp_H2O_HX= CP_H2O(T_ave_hh);
Cp_H2= CP_H2(T_H2);
Cp_O2= CP_O2(T_O2);
%Calculating the equation and parameters for different recycle ratio

for i=1:21

syms m_CO2_prod m_CO2 n_CO2_r n_H2 m_H2 n_O2 m_O2 m_cal m_H2O E_el E_out E_in E_cal E_el_t w_CaCO3 M_CO2...
     ..M_CaCO3 M_H2 M_O2 M_H2O m_RM f m_CO2_recy m_RM etta Cp_CO2_cal m_cal Cp_CaO T_cal T_ref Cp_RM T_RM...
     ..Cp_CO2_recy Cp_H2O H_cal T_CO2_recy;

%Parameters

M_CO2= 44.009e-3;          %molar mass of CO2[Kg/mol]
M_CaCO3= 100.0869e-3;      %molar mass of CaCO3[Kg/mol]
M_H2 = 1.00794e-3;         %molar mass of H2[Kg/mol]
M_O2 = 31.9988e-3;         %molar mass of O2[Kg/mol]
M_H2O= 18e-3;              %molar mass of H2O[Kg/mol]
Cp_CaO= 0.935e3;           %Specific heat capacity of CaO at 900°C [J/kg.K]
Cp_RM= 1.26e3;             %Specific heat capacity of CaCO3 at 658°C [J/kg.K]

%Function for calculation specific heat at constant pressure of CO2
Cp_CO2_cal= CP_CO2(1173);  %Specific heat capacity of CO2 at 900°C [J/kg.K]
Cp_CO2_recy= CP_CO2(323);  %Specific heat capacity of CO2 at 50°C [J/kg.K]
Cp_H2O= CP_H2O(1173);      %Specific heat capacity of H2O at 900°C [J/kg.K]

%Design Basis Values
w_CaCO3= 0.77;             %Caco3 content in a raw meal [-]
m_RM= 210;                 %Raw meal rate [t/h]
f= 0.94;                   %Degree of calcination [-]
```



```
etta= 0.8;                 %Electricity to heat conversion efficiency [-]
T_cal= 1173.15;            %Calcination temperature [K]
T_ref= 298.15;             %Reference temperature [K]
T_RM= 931.15;              %Temperature of preheated meal [K]
T_CO2_recy= 323.15;        %Temperature of recycled CO2 [K]
H_cal= -3.6e6;             %Enthalpy of calcination [J/kgCO2]
m_air= 71;                 %Mass flow rate of air [t/h]
Cp_air= 1.02867e3;         %Specific heat capacity of air at 225°C [J/kg.K]
delta_T_HX= 100;           %Minimum temperature difference of heat exchanger [K]
T_air_in= 498.15;          %Temperature of air from clinker cooker [K]
E_el_kg_H2= 39.49;         %Energy required to produce 1 kg of hydrogen[kWh]

%Mass and Energy balance equation for calcination
Eq1= m_CO2_prod== (w_CaCO3*(M_CO2/M_CaCO3)*(m_RM)*f);                  %CO2 outlet rate [t/h]
Eq2= m_CO2_recy== m_CO2_prod*r;                                         %CO2 recycling rate [t/h]
Eq3= m_CO2== m_CO2_prod + m_CO2_recy;                                   %Total CO2 rate [t/h]
Eq4= n_CO2_r== m_CO2_recy/(M_CO2*0.001);                                %Total number of moles of recycle CO2 [mol/h]
Eq5= n_H2== n_CO2_r/x_CO2;                                              %Number of moles of Hydrogen required [mol/h]
Eq6= m_H2== n_H2*(M_H2/1000);                                           %Flow rate of hydrogen[t/h]
Eq7= n_O2== (0.5/x_CO2)*n_CO2_r;                                        %Number of moles of Oxygen required[mol/h]
Eq8= m_O2== n_O2*(M_O2/1000);                                           %Flow rate of Oxygen[t/h]
Eq9= m_cal== m_RM - (m_CO2_prod);                                       %Calcined meal rate [t/h]
Eq10= m_H2O== n_H2*(M_H2O/1000);
Eq11= E_out== (m_CO2*Cp_CO2_cal + m_cal*Cp_CaO + m_H2O*Cp_H2O)*(T_cal-T_ref)*(1000/3600); %Outlet energy
Eq12= E_in== (m_RM*Cp_RM *(T_RM-T_ref)+ m_H2*Cp_H2*(T_H2-T_ref)+ m_O2*Cp_O2*(T_O2-T_ref)+ m_CO2_recy*Cp_CO2_recy*...
              ...(T_CO2_recy-T_ref))*(1000/3600);                                         %Inlet Energy
Eq13= E_cal== (m_CO2_prod*H_cal)*(1000/3600);                                             %Precalcination
Eq14= E_el== (E_el_kg_H2/etta)*(m_H2*1000);                  %Electrical energy required for water electrolysis
Eq15= E_el_t== (E_out-E_in-E_cal-E_el)/(10^6);               %Total Electrical energy required [MW]
[m_CO2_prod,m_CO2_recy,m_CO2,n_CO2_r,n_H2,m_H2,n_O2,m_O2,m_cal,m_H2O,E_out,E_in,E_cal,E_el,E_el_t]= vpasolve([Eq1,
     Eq2,Eq3,Eq4,Eq5,Eq6,Eq7,Eq8,Eq9,Eq10,Eq11,Eq12,Eq13,Eq14,Eq15],[m_CO2_prod,m_CO2_recy,m_CO2,n_CO2_r,n_H2,m_H2,
     n_O2,m_O2,m_cal,m_H2O,E_out,E_in,E_cal,E_el,E_el_t])


%Heat Exchanger
delta=10;                               %Iteration limit

while delta>=1
    C_air= m_air*Cp_air_HX
    C_CO2= m_CO2*Cp_CO2_HX
    C_H2O= m_H2O*Cp_H2O_HX

    if C_air>=(C_CO2+C_H2O)
```

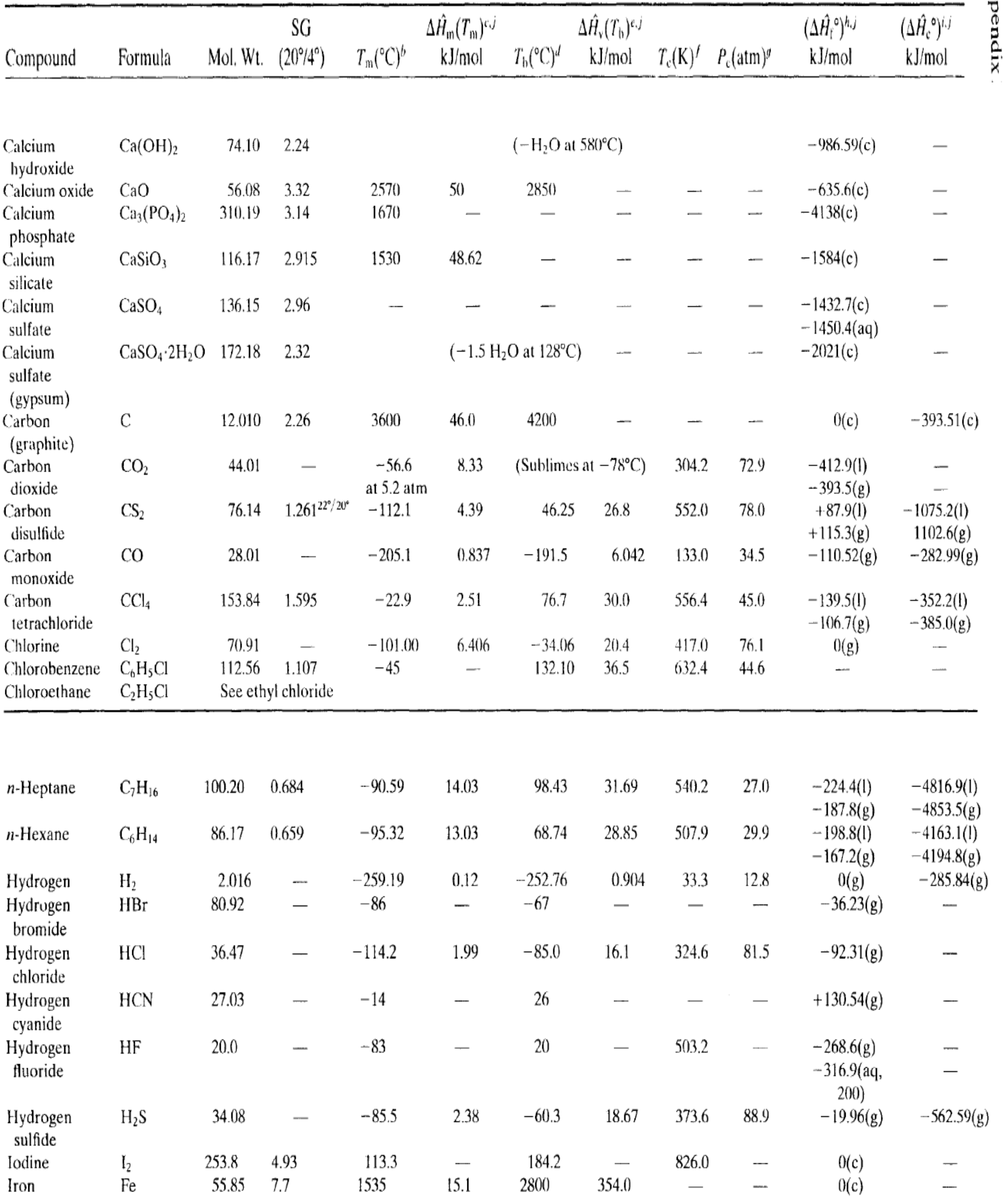
```
        T_CO2_out= T_air_in+ delta_T_HX;      %Outlet temperature of CO2 [K]
        T_H2O_out= T_air_in+ delta_T_HX;      %Oulet temperature of H2O [K]
        T_CO2_ave= (T_CO2_out + T_cal)/2;     %Average temperature of CO2 [K]
        T_H2O_ave= (T_H2O_out + T_cal)/2;     %Average temperature of H2O [K]
        Cp_CO2_HX= CP_CO2(T_CO2_ave);         %Defining specific heat of hot side based on average temperature [J/kg.K]
        Cp_H2O_HX= CP_H2O(T_H2O_ave);         %Defining specific heat of hot side based on average temperature [J/kg.K]
        T_air_out_old= T_air_in + (((m_CO2*Cp_CO2_HX)+(m_H2O*Cp_H2O_HX))*(T_cal-T_CO2_out))/(m_air*Cp_air_HX);
                                              %Determining outlet temprature of air [K]

        T_ave_air= (T_air_out_old+T_air_in)/2;    %Defining average temperature of cold side [K]
        Cp_air_HX= CP_air(T_ave_air);             %Defining specific heat of air stream [J/kg.K]
        T_air_out_new= T_air_in + (((m_CO2*Cp_CO2_HX)+(m_H2O*Cp_H2O_HX))*(T_cal-T_CO2_out))/(m_air*Cp_air_HX);
                                                  %Determining new outlet temperature of air [K]
        delta= T_air_out_new-T_air_out_old;

    else
        T_air_out= T_cal- delta_T_HX;
        T_aver_air= (T_air_in+T_air_out)/2;
        Cp_air_HX= CP_air(T_aver_air);
        T_CO2_H2O_out_old= T_cal-(m_air*Cp_air_HX*(T_air_out-T_air_in))/((m_CO2*Cp_CO2_HX)+(m_H2O*Cp_H2O_HX));
        T_CO2_H2O_ave= (T_cal+T_CO2_H2O_out_old)/2;
        Cp_CO2_HX= CP_CO2(T_CO2_H2O_ave);
        Cp_H2O_HX= CP_H2O(T_CO2_H2O_ave);
        T_CO2_H2O_out_new= T_cal-(m_air*Cp_air_HX*(T_air_out-T_air_in))/((m_CO2*Cp_CO2_HX)+(m_H2O*Cp_H2O_HX));
        delta= T_CO2_H2O_out_new-T_CO2_H2O_out_old;

    end
end
a(i)= m_CO2;
c(i)= m_cal;
d(i)= E_el_t;
e(i)= T_CO2_H2O_out_new;
b(i)=r;
r=r+0.05;
end

%Plotting
format short
figure(1)
plot(b,a,'*g','linewidth',2)
xlim([0 1]);
title('CO2 outlet rate')
```



```
xlabel('CO2 recycle ratio [-]')
ylabel('CO2 exit rate [t/h]')

figure(2)
plot(b,d,'-.m','linewidth',3)
xlim([0 1]);
title('Electrical energy')
xlabel('CO2 recycle ratio [-]')
ylabel('Electrical energy [MW]')

figure(3)
plot(b,e,'c','linewidth',3)
xlim([0 1]);
title('CO2&H2O outlet temperature')
xlabel('CO2 recycle ratio [-]')
ylabel('CO2&H2O outlet temperature [K]')
```

Appendix D: Thermodynamics physical property table

Table B.1 Selected Physical Property Data[a]



Appendix

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)$[c,j] kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)$[e,j] kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f^\circ)$[h,j] kJ/mol	$(\Delta\hat{H}_c^\circ)$[i,j] kJ/mol
Calcium hydroxide	$Ca(OH)_2$	74.10	2.24			(−H_2O at 580°C)				−986.59(c)	—
Calcium oxide	CaO	56.08	3.32	2570	50	2850	—	—	—	−635.6(c)	—
Calcium phosphate	$Ca_3(PO_4)_2$	310.19	3.14	1670	—	—	—	—	—	−4138(c)	—
Calcium silicate	$CaSiO_3$	116.17	2.915	1530	48.62	—	—	—	—	−1584(c)	—
Calcium sulfate	$CaSO_4$	136.15	2.96	—	—	—	—	—	—	−1432.7(c) −1450.4(aq)	—
Calcium sulfate (gypsum)	$CaSO_4 \cdot 2H_2O$	172.18	2.32		(−1.5 H_2O at 128°C)		—	—	—	−2021(c)	—
Carbon (graphite)	C	12.010	2.26	3600	46.0	4200	—	—	—	0(c)	−393.51(c)
Carbon dioxide	CO_2	44.01	—	−56.6 at 5.2 atm	8.33	(Sublimes at −78°C)		304.2	72.9	−412.9(l) −393.5(g)	— —
Carbon disulfide	CS_2	76.14	$1.261^{22°/20°}$	−112.1	4.39	46.25	26.8	552.0	78.0	+87.9(l) +115.3(g)	−1075.2(l) 1102.6(g)
Carbon monoxide	CO	28.01	—	−205.1	0.837	−191.5	6.042	133.0	34.5	−110.52(g)	−282.99(g)
Carbon tetrachloride	CCl_4	153.84	1.595	−22.9	2.51	76.7	30.0	556.4	45.0	−139.5(l) −106.7(g)	−352.2(l) −385.0(g)
Chlorine	Cl_2	70.91	—	−101.00	6.406	−34.06	20.4	417.0	76.1	0(g)	—
Chlorobenzene	C_6H_5Cl	112.56	1.107	−45	—	132.10	36.5	632.4	44.6	—	—
Chloroethane	C_2H_5Cl	See ethyl chloride									
n-Heptane	C_7H_{16}	100.20	0.684	−90.59	14.03	98.43	31.69	540.2	27.0	−224.4(l) −187.8(g)	−4816.9(l) −4853.5(g)
n-Hexane	C_6H_{14}	86.17	0.659	−95.32	13.03	68.74	28.85	507.9	29.9	−198.8(l) −167.2(g)	−4163.1(l) −4194.8(g)
Hydrogen	H_2	2.016	—	−259.19	0.12	−252.76	0.904	33.3	12.8	0(g)	−285.84(g)
Hydrogen bromide	HBr	80.92	—	−86	—	−67	—	—	—	−36.23(g)	—
Hydrogen chloride	HCl	36.47	—	−114.2	1.99	−85.0	16.1	324.6	81.5	−92.31(g)	—
Hydrogen cyanide	HCN	27.03	—	−14	—	26	—	—	—	+130.54(g)	—
Hydrogen fluoride	HF	20.0	—	−83	—	20	—	503.2	—	−268.6(g) −316.9(aq, 200)	— —
Hydrogen sulfide	H_2S	34.08	—	−85.5	2.38	−60.3	18.67	373.6	88.9	−19.96(g)	−562.59(g)
Iodine	I_2	253.8	4.93	113.3	—	184.2	—	826.0	—	0(c)	—
Iron	Fe	55.85	7.7	1535	15.1	2800	354.0	—	—	0(c)	—

Table B.2 Heat Capacities[a]

Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^{-2}$

Example: $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	°C	123.0	18.6			−30–60
			g	1	°C	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
Ammonia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	°C	126.5	23.4			6–67
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
n-Butane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	°C	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373
Carbon dioxide	CO_2	44.01	g	1	°C	36.11	4.233	−2.887	7.464	0–1500
Carbon monoxide	CO	28.01	g	1	°C	28.95	0.4110	0.3548	−2.220	0–1500
Carbon tetrachloride	CCl_4	153.84	l	1	K	93.39	12.98			273–343
Chlorine	Cl_2	70.91	g	1	°C	33.60	1.367	−1.607	6.473	0–1200
Copper	Cu	63.54	c	1	K	22.76	0.6117			273–1357

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[a] Adapted in part from D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering,* 3rd Edition, © 1974, Table E.1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

Table B.2 (Continued)

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Cumene (Isopropyl benzene)	C_9H_{12}	120.19	g	1	°C	139.2	53.76	−39.79	120.5	0–1200
Cyclohexane	C_6H_{12}	84.16	g	1	°C	94.140	49.62	−31.90	80.63	0–1200
Cyclopentane	C_5H_{10}	70.13	g	1	°C	73.39	39.28	−25.54	68.66	0–1200
Ethane	C_2H_6	30.07	g	1	°C	49.37	13.92	−5.816	7.280	0–1200
Ethyl alcohol (Ethanol)	C_2H_5OH	46.07	l	1	°C	103.1				0
			l	1	°C	158.8				100
			g	1	°C	61.34	15.72	−8.749	19.83	0–1200
Ethylene	C_2H_4	28.05	g	1	°C	+40.75	11.47	−6.891	17.66	0–1200
Ferric oxide	Fe_2O_3	159.70	c	2	K	103.4	6.711	-17.72×10^{10}	—	273–1097
Formaldehyde	CH_2O	30.03	g	1	°C	34.28	4.268	0.0000	−8.694	0–1200
Helium	He	4.00	g	1	°C	20.8				0–1200
n-Hexane	C_6H_{14}	86.17	l	1	°C	216.3				20–100
			g	1	°C	137.44	40.85	−23.92	57.66	0–1200
Hydrogen	H_2	2.016	g	1	°C	28.84	0.00765	0.3288	−0.8698	0–1500
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	−0.0227	0.9887	−4.858	0–1200
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	−0.1341	0.9715	−4.335	0–1200
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0–1200
Hydrogen sulfide	H_2S	34.08	g	1	°C	33.51	1.547	0.3012	−3.292	0–1500
Magnesium chloride	$MgCl_2$	95.23	c	1	K	72.4	1.58			273–991
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	-8.732×10^{10}		273–2073
Methane	CH_4	16.04	g	1	°C	34.31	5.469	0.3661	−11.00	0–1200
			g	1	K	19.87	5.021	1.268	−11.00	273–1500
Methyl alcohol (Methanol)	CH_3OH	32.04	l	1	°C	75.86	16.83			0–65
			g	1	°C	42.93	8.301	−1.87	−8.03	0–700
Methyl cyclohexane	C_7H_{14}	98.18	g	1	°C	121.3	56.53	−37.72	100.8	0–1200
Methyl cyclopentane	C_6H_{12}	84.16	g	1	°C	98.83	45.857	−30.44	83.81	0–1200
Nitric acid	NHO_3	63.02	l	1	°C	110.0				25
Nitric oxide	NO	30.01	g	1	°C	29.50	0.8188	−0.2925	0.3652	0–3500

Nitrogen	N_2	28.02	g	1	°C	29.00	0.2199	0.5723	−2.871	0–1500
Nitrogen dioxide	NO_2	46.01	g	1	°C	36.07	3.97	−2.88	7.87	0–1200
Nitrogen tetraoxide	N_2O_4	92.02	g	1	°C	75.7	12.5	−11.3		0–300
Nitrous oxide	N_2O	44.02	g	1	°C	37.66	4.151	−2.694	10.57	0–1200
Oxygen	O_2	32.00	g	1	°C	29.10	1.158	−0.6076	1.311	0–1500
n-Pentane	C_5H_{12}	72.15	l	1	°C	155.4	43.68			0–36
			g	1	°C	114.8	34.09	−18.99	42.26	0–1200
Propane	C_3H_8	44.09	g	1	°C	68.032	22.59	−13.11	31.71	0–1200
Propylene	C_3H_6	42.08	g	1	°C	59.580	17.71	−10.17	24.60	0–1200
Sodium carbonate	Na_2CO_3	105.99	c	1	K	121				288–371
Sodium carbonate decahydrate	$Na_2CO_3 \cdot 10H_2O$	286.15	c	1	K	535.6				298
Sulfur	S	32.07	c (Rhombic)	1	K	15.2	2.68			273–368
			c (Monoclinic)	1	K	18.3	1.84			368–392
Sulfuric acid	H_2SO_4	98.08	l	1	°C	139.1	15.59			10–45
Sulfur dioxide	SO_2	64.07	g	1	°C	38.91	3.904	−3.104	8.606	0–1500
Sulfur trioxide	SO_3	80.07	g	1	°C	48.50	9.188	−8.540	32.40	0–1000
Toluene	C_7H_8	92.13	l	1	°C	148.8	32.4			0–110
			g	1	°C	94.18	38.00	−27.86	80.33	0–1200
Water	H_2O	18.016	l	1	°C	75.4				0–100
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

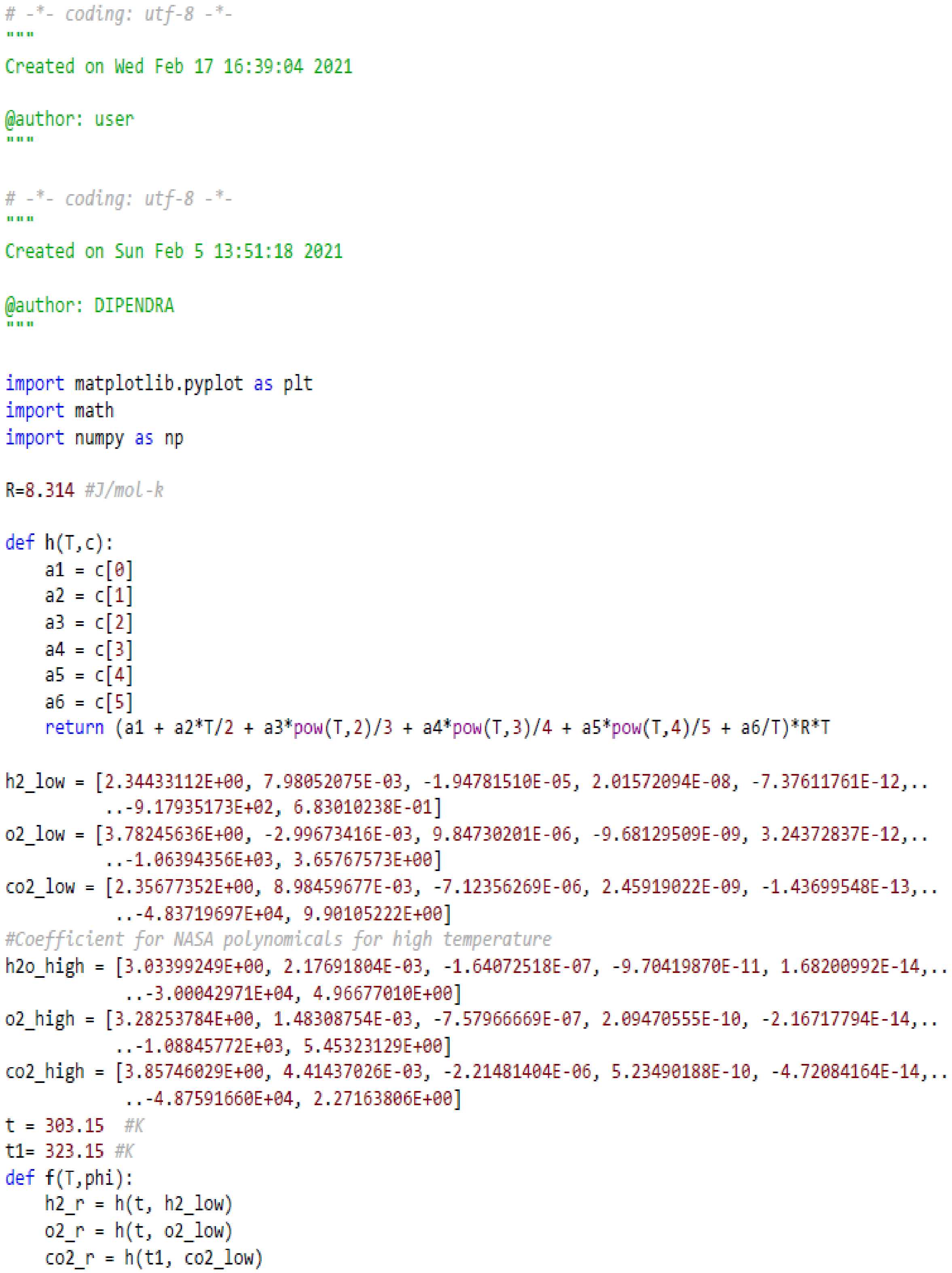
Table B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)

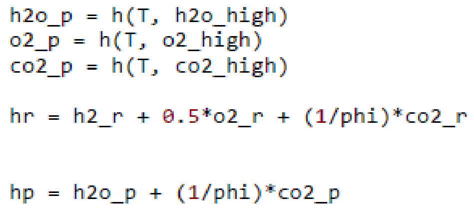
Reference state: Gas, $P_{ref} = 1$ atm, $T_{ref} = 25°C$

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01
600	17.55	18.41	17.39	16.81	17.57	26.53	20.91
700	20.80	21.86	20.59	19.81	20.82	31.88	24.92
800	24.10	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

Appendix E: Python code to calculate adiabatic flame temperature



```
# -*- coding: utf-8 -*-
"""
Created on Wed Feb 17 16:39:04 2021

@author: user
"""

# -*- coding: utf-8 -*-
"""
Created on Sun Feb 5 13:51:18 2021

@author: DIPENDRA
"""

import matplotlib.pyplot as plt
import math
import numpy as np

R=8.314 #J/mol-k

def h(T,c):
    a1 = c[0]
    a2 = c[1]
    a3 = c[2]
    a4 = c[3]
    a5 = c[4]
    a6 = c[5]
    return (a1 + a2*T/2 + a3*pow(T,2)/3 + a4*pow(T,3)/4 + a5*pow(T,4)/5 + a6/T)*R*T

h2_low = [2.34433112E+00, 7.98052075E-03, -1.94781510E-05, 2.01572094E-08, -7.37611761E-12,..
          ..-9.17935173E+02, 6.83010238E-01]
o2_low = [3.78245636E+00, -2.99673416E-03, 9.84730201E-06, -9.68129509E-09, 3.24372837E-12,..
          ..-1.06394356E+03, 3.65767573E+00]
co2_low = [2.35677352E+00, 8.98459677E-03, -7.12356269E-06, 2.45919022E-09, -1.43699548E-13,..
           ..-4.83719697E+04, 9.90105222E+00]
#Coefficient for NASA polynomicals for high temperature
h2o_high = [3.03399249E+00, 2.17691804E-03, -1.64072518E-07, -9.70419870E-11, 1.68200992E-14,..
            ..-3.00042971E+04, 4.96677010E+00]
o2_high = [3.28253784E+00, 1.48308754E-03, -7.57966669E-07, 2.09470555E-10, -2.16717794E-14,..
           ..-1.08845772E+03, 5.45323129E+00]
co2_high = [3.85746029E+00, 4.41437026E-03, -2.21481404E-06, 5.23490188E-10, -4.72084164E-14,..
            ..-4.87591660E+04, 2.27163806E+00]
t = 303.15  #K
t1= 323.15 #K
def f(T,phi):
    h2_r = h(t, h2_low)
    o2_r = h(t, o2_low)
    co2_r = h(t1, co2_low)
```



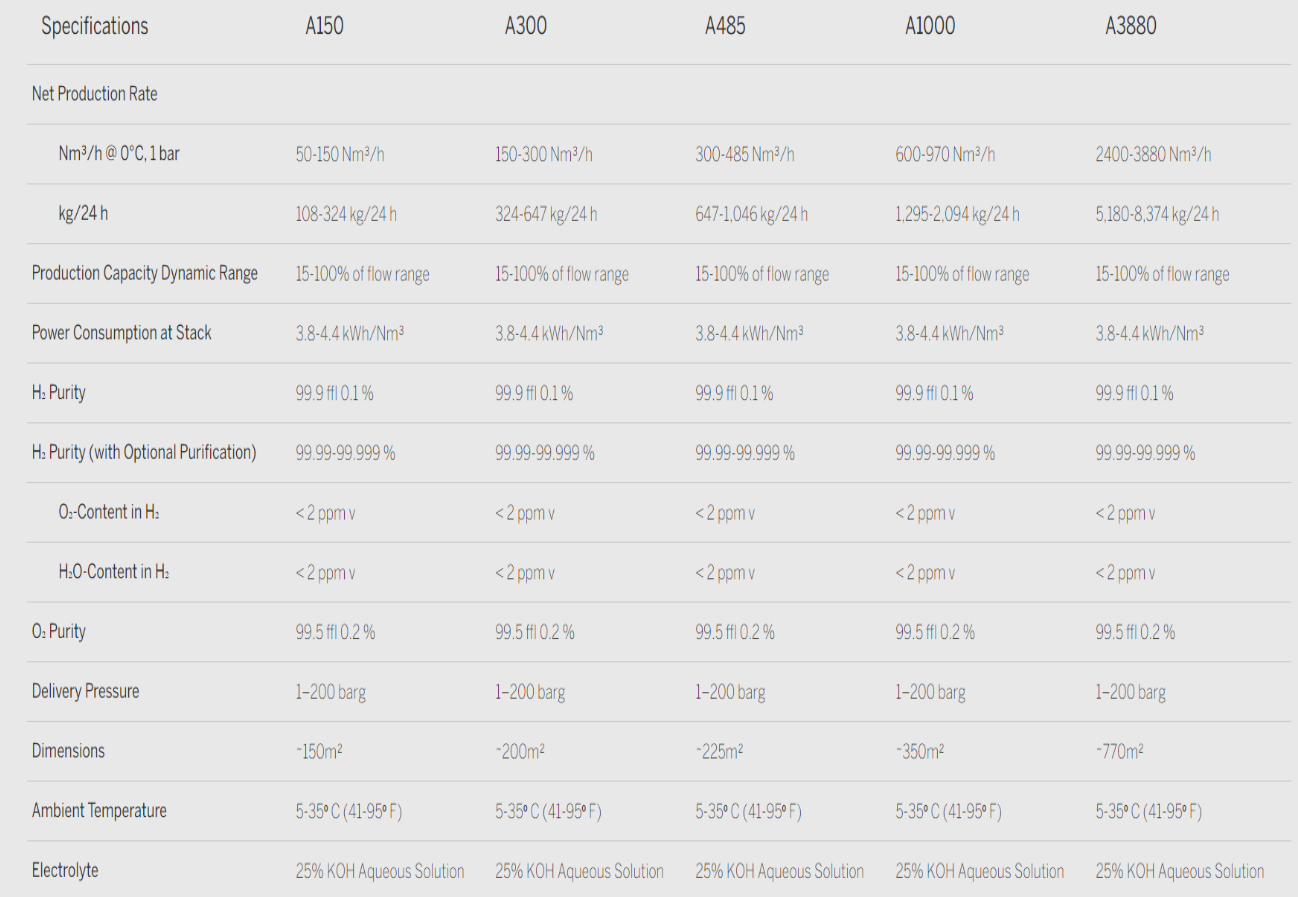
```
h2o_p = h(T, h2o_high)
o2_p = h(T, o2_high)
co2_p = h(T, co2_high)

hr = h2_r + 0.5*o2_r + (1/phi)*co2_r


hp = h2o_p + (1/phi)*co2_p
```

```
    H= (hp-hr)
    return H

def fprime(T,phi):
    return(f(T+1e-6,phi)-f(T,phi))/1e-6

Tguess = 1500
T_aft = []
tol = 1e-6
phi = np.linspace(0.2,1,num=10)
itr = []
a= 0.8

for i in range(0,len(phi)):
    ctr= 0
    while(abs(f(Tguess,phi[i]))>tol):
        Tguess = Tguess - a*(f(Tguess,phi[i])/fprime(Tguess,phi[i]))
        ctr= ctr+1
    T_aft.append(Tguess)
    itr.append(ctr)

plt.plot(phi,T_aft,'-o', color='red')
plt.title('AFT vs Equivalence ratio')
plt.xlabel('Equivalence ratio')
plt.ylabel('Adiabatic Flame Temperature(K)')
plt.legend()
plt.grid('on')
plt.show()
```

Appendix F: NASA polynomials

```
THERMO
   300.000  1000.000  5000.000
! GRI-Mech Version 3.0 Thermodynamics released 7/30/99
! NASA Polynomial format for CHEMKIN-II
! see README file for disclaimer
O                 L 1/90O   1               G   200.000  3500.000  1000.000    1
 2.56942078E+00-8.59741137E-05 4.19484589E-08-1.00177799E-11 1.22833691E-15    2
 2.92175791E+04 4.78433864E+00 3.16826710E+00-3.27931884E-03 6.64306396E-06    3
-6.12806624E-09 2.11265971E-12 2.91222592E+04 2.05193346E+00                   4
O2                TPIS89O   2               G   200.000  3500.000  1000.000    1
 3.28253784E+00 1.48308754E-03-7.57966669E-07 2.09470555E-10-2.16717794E-14    2
-1.08845772E+03 5.45323129E+00 3.78245636E+00-2.99673416E-03 9.84730201E-06    3
-9.68129509E-09 3.24372837E-12-1.06394356E+03 3.65767573E+00                   4
H                 L 7/88H   1               G   200.000  3500.000  1000.000    1
 2.50000001E+00-2.30842973E-11 1.61561948E-14-4.73515235E-18 4.98197357E-22    2
 2.54736599E+04-4.46682914E-01 2.50000000E+00 7.05332819E-13-1.99591964E-15    3
 2.30081632E-18-9.27732332E-22 2.54736599E+04-4.46682853E-01                   4
H2                TPIS78H   2               G   200.000  3500.000  1000.000    1
 3.33727920E+00-4.94024731E-05 4.99456778E-07-1.79566394E-10 2.00255376E-14    2
-9.50158922E+02-3.20502331E+00 2.34433112E+00 7.98052075E-03-1.94781510E-05    3
 2.01572094E-08-7.37611761E-12-9.17935173E+02 6.83010238E-01                   4
OH                RUS 78O   1H   1          G   200.000  3500.000  1000.000    1
 3.09288767E+00 5.48429716E-04 1.26505228E-07-8.79461556E-11 1.17412376E-14    2
 3.85865700E+03 4.47669610E+00 3.99201543E+00-2.40131752E-03 4.61793841E-06    3
-3.88113333E-09 1.36411470E-12 3.61508056E+03-1.03925458E-01                   4
H2O               L 8/89H   2O   1          G   200.000  3500.000  1000.000    1
 3.03399249E+00 2.17691804E-03-1.64072518E-07-9.70419870E-11 1.68200992E-14    2
-3.00042971E+04 4.96677010E+00 4.19864056E+00-2.03643410E-03 6.52040211E-06    3
-5.48797062E-09 1.77197817E-12-3.02937267E+04-8.49032208E-01                   4

CO2               L 7/88C   1O   2          G   200.000  3500.000  1000.000    1
 3.85746029E+00 4.41437026E-03-2.21481404E-06 5.23490188E-10-4.72084164E-14    2
-4.87591660E+04 2.27163806E+00 2.35677352E+00 8.98459677E-03-7.12356269E-06    3
 2.45919022E-09-1.43699548E-13-4.83719697E+04 9.90105222E+00                   4
HCO               L12/89H   1C   1O   1     G   200.000  3500.000  1000.000    1
 2.77217438E+00 4.95695526E-03-2.48445613E-06 5.89161778E-10-5.33508711E-14    2
 4.01191815E+03 9.79834492E+00 4.22118584E+00-3.24392532E-03 1.37799446E-05    3
-1.33144093E-08 4.33768865E-12 3.83956496E+03 3.39437243E+00                   4
CH2O              L 8/88H   2C   1O   1     G   200.000  3500.000  1000.000    1
 1.76069008E+00 9.20000082E-03-4.42258813E-06 1.00641212E-09-8.83855640E-14    2
-1.39958323E+04 1.36563230E+01 4.79372315E+00-9.90833369E-03 3.73220008E-05    3
-3.79285261E-08 1.31772652E-11-1.43089567E+04 6.02812900E-01                   4
```

Appendix G: Models and specifications of atmospheric alkaline water electrolyzers



Specifications	A150	A300	A485	A1000	A3880
Net Production Rate					
Nm^3/h @ 0°C, 1 bar	50-150 Nm^3/h	150-300 Nm^3/h	300-485 Nm^3/h	600-970 Nm^3/h	2400-3880 Nm^3/h
kg/24 h	108-324 kg/24 h	324-647 kg/24 h	647-1,046 kg/24 h	1,295-2,094 kg/24 h	5,180-8,374 kg/24 h
Production Capacity Dynamic Range	15-100% of flow range	15-100% of flow range	15-100% of flow range	15-100% of flow range	15-100% of flow range
Power Consumption at Stack	3.8-4.4 kWh/Nm^3	3.8-4.4 kWh/Nm^3	3.8-4.4 kWh/Nm^3	3.8-4.4 kWh/Nm^3	3.8-4.4 kWh/Nm^3
H_2 Purity	99.9 ffl 0.1 %	99.9 ffl 0.1 %	99.9 ffl 0.1 %	99.9 ffl 0.1 %	99.9 ffl 0.1 %
H_2 Purity (with Optional Purification)	99.99-99.999 %	99.99-99.999 %	99.99-99.999 %	99.99-99.999 %	99.99-99.999 %
O_2-Content in H_2	< 2 ppm v	< 2 ppm v	< 2 ppm v	< 2 ppm v	< 2 ppm v
H_2O-Content in H_2	< 2 ppm v	< 2 ppm v	< 2 ppm v	< 2 ppm v	< 2 ppm v
O_2 Purity	99.5 ffl 0.2 %	99.5 ffl 0.2 %	99.5 ffl 0.2 %	99.5 ffl 0.2 %	99.5 ffl 0.2 %
Delivery Pressure	1–200 barg	1–200 barg	1–200 barg	1–200 barg	1–200 barg
Dimensions	~150m^2	~200m^2	~225m^2	~350m^2	~770m^2
Ambient Temperature	5-35° C (41-95° F)	5-35° C (41-95° F)	5-35° C (41-95° F)	5-35° C (41-95° F)	5-35° C (41-95° F)
Electrolyte	25% KOH Aqueous Solution	25% KOH Aqueous Solution	25% KOH Aqueous Solution	25% KOH Aqueous Solution	25% KOH Aqueous Solution

Appendix H: Cost estimation calculation with recycle ratio 0.1

1. Calculating required of CO_2 recycle rate, $Q_{CO_2,r}$

$$\dot{m}_{CO_2,r} = 6.683 \text{ t/h}$$

$$Q_{CO_2,r} = \frac{\dot{m}_{CO_2,r}}{\rho_{CO_2}} = \frac{6.683}{0.4515} \times \left(\frac{1000}{3600}\right) = 4.11\, m^3/s$$

2. Calculating required amount of hydrogen and oxygen fuel, (refer to sub-chapter 3.2.2.1)

$$\dot{m}_{H_2} = 174.53 \left[\frac{kg}{h}\right] = 4188.72 \left[\frac{kg}{day}\right]$$

$$\dot{m}_{O_2} = 1385.13 \left[\frac{kg}{h}\right] = 33243.12 \left[\frac{kg}{day}\right]$$

3. Choosing commercial water electrolysis,

Model Alkaline water electrolysis of model A485 (refer to Appendix G).

Production rate of hydrogen ($\dot{m}_{H_2,A485}$) = 1046 kg/day

Number of electrolysis cell required (N_{ec}) = $\frac{\dot{m}_{H_2}}{\dot{m}_{H_2,A485}} \approx 4$

4. Determining the total installation cost for water electrolyzer,

Model A485 specification,

Net production rate of hydrogen ($\dot{P}_{H_2}$)= 485 Nm^3/h

Power consumption (ε_c)= 4.4 kWh/Nm^3

$$\varepsilon_{el,we} = N_{ec} \cdot \dot{P}_{H_2} \cdot \varepsilon_c = 4 \times 1046 \times 4.4 = 18409.6\, kW = 18.409\, MW$$

Therefore, the total installation cost of water electrolyzer is ($430 \times 18409.6 = 7.916$ MUSD)

5. Installation cost of CO_2 fan

The price of centrifugal radial fan based on the volumetric capacity for CO_2 recycling ($Q_{CO_2,r} = 4.11\ \text{m}^3/\text{s}$) is 4711 USD (refer to sub-chapter 6.1.3)

6. Adjusting the currency

The currency exchange rate from USD to NOK is 8.25. (refer to sub-chapter 6.3)

Equipment	Model	Capacity	Unit	Year	Currency	Cost

Water Electrolyzer	A485	485, N_{ec}=4	Nm^3/h	2011	MNOK	65.307
Centrifugal radial fan	--------	4.11	m^3/s	2002	kNOK	38.865

7. Adjusting the time

Refer to sub-chapter (6.3)

Equipment	Model	Capacity	Unit	Year	Currency	Cost
Water Electrolyzer	A485	485, N_{ec}=4	Nm^3/h	2021	MNOK	77.519
Centrifugal radial fan	--------	24.47	m^3/s	2021	kNOK	57.675
Total installation cost	------	------	-----	2021	MNOK	77.576

8. Determining equivalent electricity cost,

$C_{el,kWh} = 0.335$ NOK/kWh

$\varepsilon_{el,we} = 18409.6$ kW

$$\therefore C_{el,yr} = C_{el,kWh} \cdot \varepsilon_{el,we} \cdot n_{h,yr} = 0.335 \times 18409.6 \times 7315$$
$$= 45.113\ MNOK/year$$

9. Calculating net present value, (refer to sub-chapter 6.6)

$$NPV = C_{el,yr} + \frac{C_{el,yr}}{(1+i)^1} + \frac{C_{el,yr}}{(1+i)^2} + \cdots + \frac{C_{el,yr}}{(1+i)^{n-1}}$$
$$= 428.08\ MNOK/year$$

10. Calculating equivalent annual cost, (refer to sub-chapter 6.7)

$$EAC_{CAPEX} = \frac{NPV_{CAPEX}}{a_f} = \frac{77.576}{8.49} = 9.14\ MNOK/year$$

$$EAC_{OPEX} = \frac{NPV_{OPEX}}{a_f} = \frac{428.08}{8.49} = 50.42\ MNOK/year$$

11. Cost per avoided CO_2 unit

Recycle ratio (r_r) = 0.1

Total amount of CO_2 avoided = $\dot{m}_{CO_2,m} - (r_r \times \dot{m}_{CO_2,m}) = \ 60.147$ [t/h]

Operation hour = 7315 [h/y]

$$\therefore \dot{m}_{CO_2,year} = 60.147 \times 7315 = 439975.305 \ \left[\frac{t}{y}\right]$$

$$CAPEX = \frac{\mathrm{EAC_{CAPEX}}}{\dot{m}_{CO_2,year}} = 20.77 \ \frac{NOK}{tCO_2 \ captured}$$

$$OPEX = \frac{\mathrm{EAC}_{OPEX}}{\dot{m}_{CO_2,year}} = \ 114.6 \ \frac{NOK}{tCO_2 \ captured}$$

Therefore, cost per avoided CO_2 unit is 135.37 $\frac{NOK}{tCO_2 \ captured}$.

This cost estimation for our modified cement calciner system is estimated excluding the capital investment cost to construct new calciner with desired diameter 2.18m as calculated in sub-chapter (4.1.1).

Appendix I: Adiabatic flame temperature plot as a result of H_2 and O_2 combustion