بسم الله الرحمن الرحيم

طاقة الشمال
North Lebanon Alternative Power
www.nlap-lb.com

AECENAR
Association for Economical and Technological Cooperation in the Euro-Asian and North-African Region
www.aecenar.com

MEAE - Middle East Alternative Energy Institute
مركز الشرق الاوسط للطاقة البديلة
http://aecenar.com/institutes/meae

NLAP-WEDC Waste to Electricity Demonstration Cycle - Project Report 2 (2018)

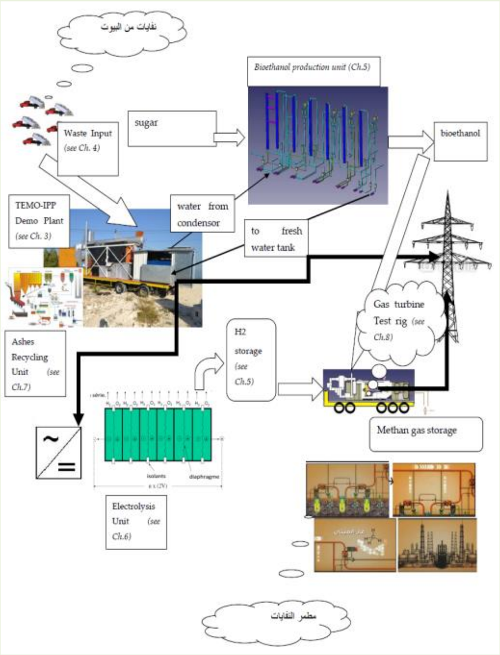
Basics:

- Heavy metals recovery
- Fly ashes treatment
- Waste Landfill Gas Utilization
- Methane liquefaction
- Electrical Systems in Power Plants
- Incinerator Safety Design and Safety Analysis
- Power Plant Materials and Corrosion
- Chemistry in Power Plant Process Systems
- Bioethanol/Distillated water (DW)

Detailed Design & Contruction for:

- NLAP-WEDC Waste to Electricity Demonstration Cycle.
- Installation of TEMO-IPP Demo Plant at Raihaniyye Refugees Camp.
- Electrolysis/Hydrogen Production Unit.
- Ashes Recycling Unit.
- H2 Burner Unit, Methane Burner Unit
- Electric valve.

Electrical Power Plant Technology



Siham Aisha (Editor)

Authors: Samir Mourad, Khaled Maoulaoui, Maysaa Kamardine, Samer Youssef, Othman Dhaybi, Maryam Abdel-Karim

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المضمون

Tables

Figures

(Introduction) مدخل

The target of MEAE-WEDC Waste to Electricity Demonstration Cycle project is to develop continously different components of a electricity generation plant using waste as energy input.

Some of the bacics (Chapter 2) and the principle system concept (Chapter 1) is from [KamNLAP 2016].

التمويل ييم منذ 2017 من قبل شركة طاقة الشمال (مكتب ابحاث 2017–2020). وقد تم من قبل هذا المكتب ابحاث تمويل النظام التحكم لمحطة 2 ميكا وات في سنة 2017.

Abbrevations:

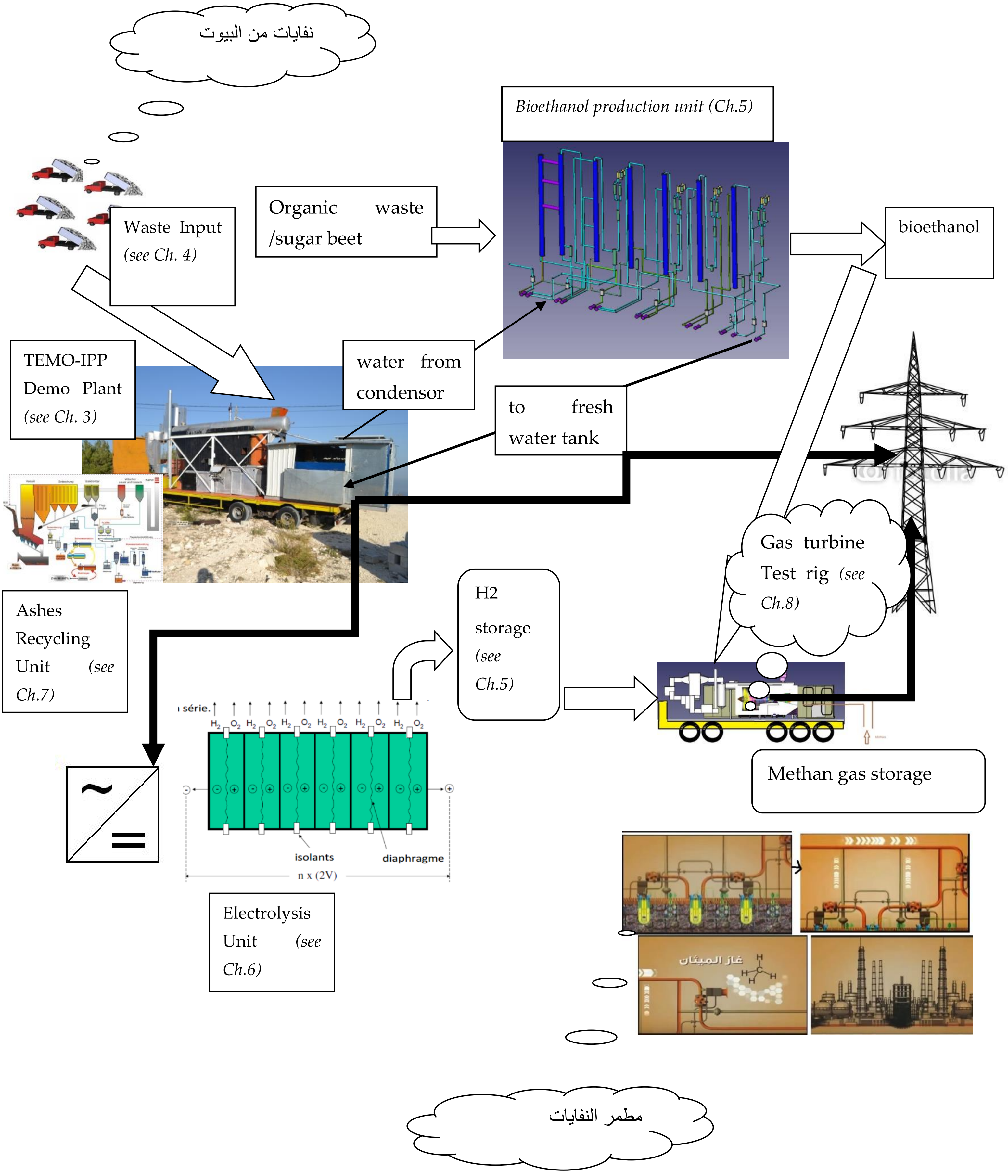
incinerator react.

nuc NE

HWPW-h.water pressurized water plant

1 نظرة عامة على منشأة (Overwiew of facility)

1.1 Components of Waste to electricity demonstration cycle



نفايات من البيوت

Bioethanol production unit (Ch.5)

Waste Input *(see Ch. 4)*

Organic waste /sugar beet

bioethanol

TEMO-IPP Demo Plant *(see Ch. 3)*

water from condensor

to fresh water tank

Gas turbine Test rig *(see Ch.8)*

H2 storage *(see Ch.5)*

Ashes Recycling Unit *(see Ch.7)*

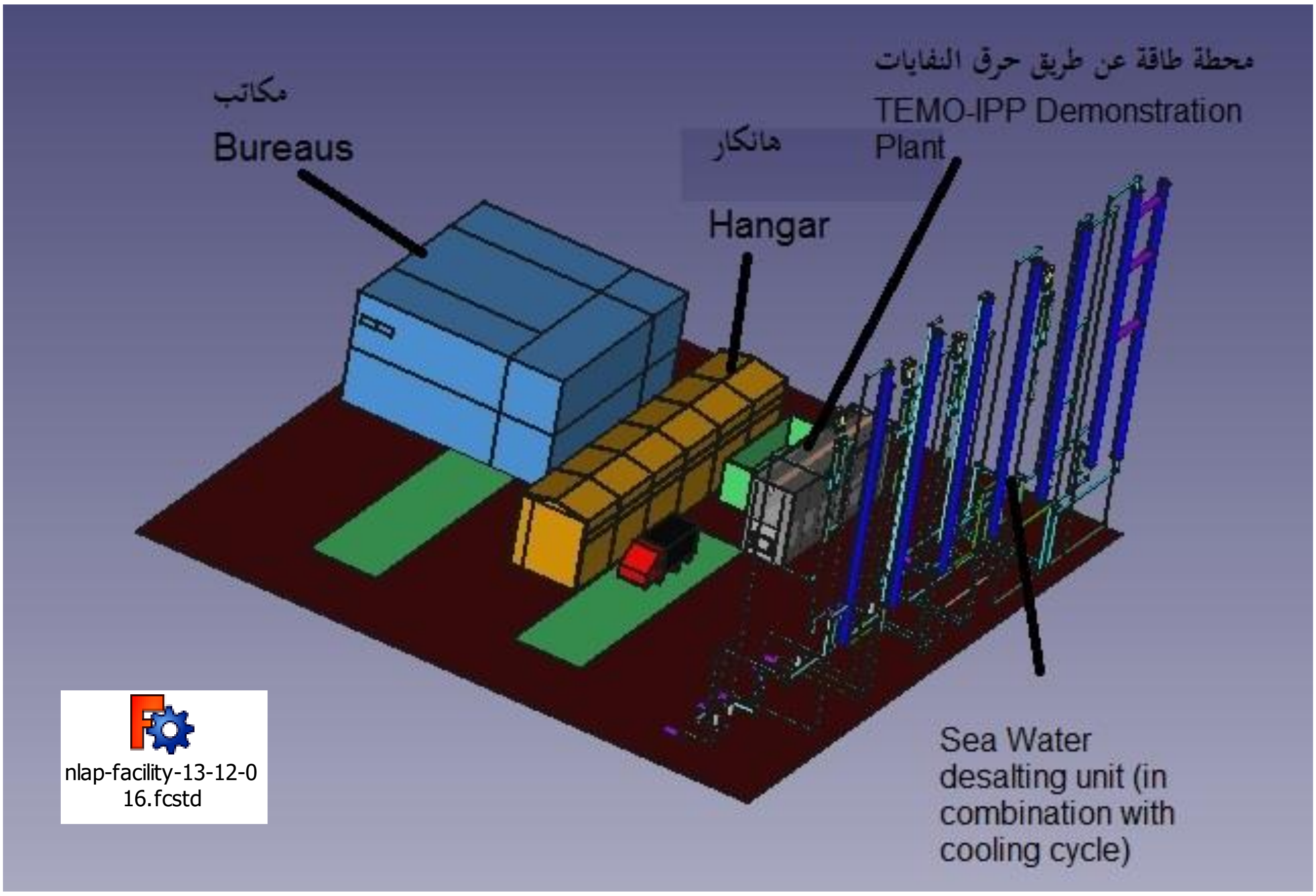
Methan gas storage

Electrolysis Unit *(see Ch.6)*

مطمر النفايات

1.2 Option 1

1.2.1 المساحة (Area) 30m x 40m



40m x 40 m = 1600 qm

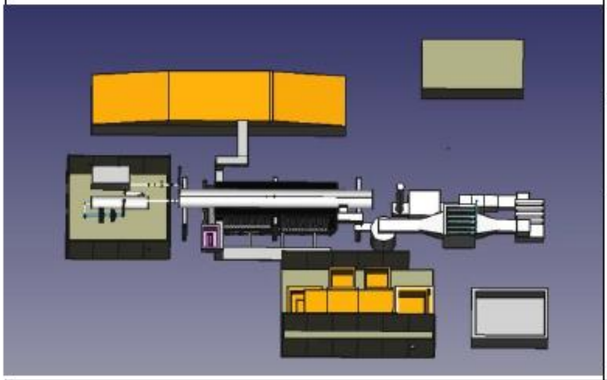
1.2.2 اجزاء الموقع

The facility has three parts:

- Waste to electricity demonstration cycle
- hangar for production of power plant devices and integration
- bureaus for engineering and administration

NLAP Incineration Demonstration power plant

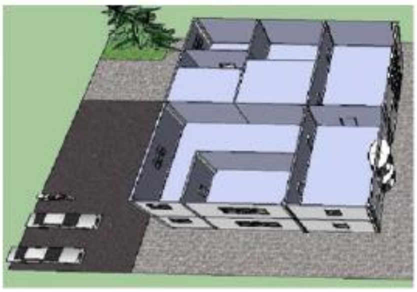
(30 m x 12m= 360 qm)



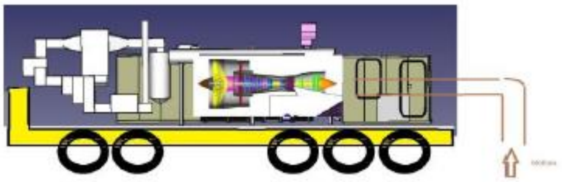
Water Tank (Cooling)

Desalting unit

Production Hangar (12m x 30 m = 300 qm)



Bureaus (15m x 15 m = 150 qm)



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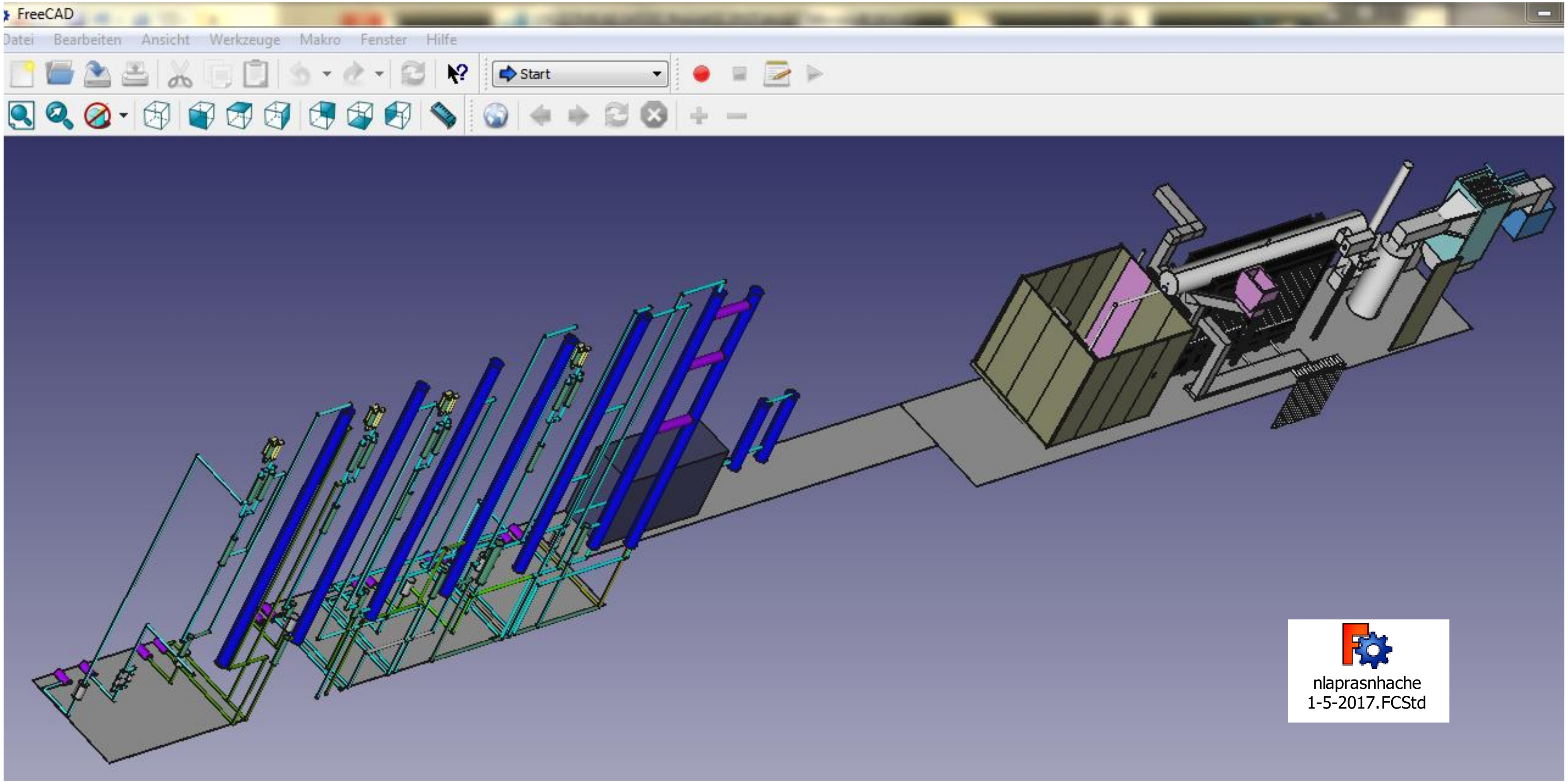
موقع مؤسسة طاقة الشمال

27m x 32 m = 864 qm

1.3 Option 2


FreeCAD
Datei
Bearbeiten
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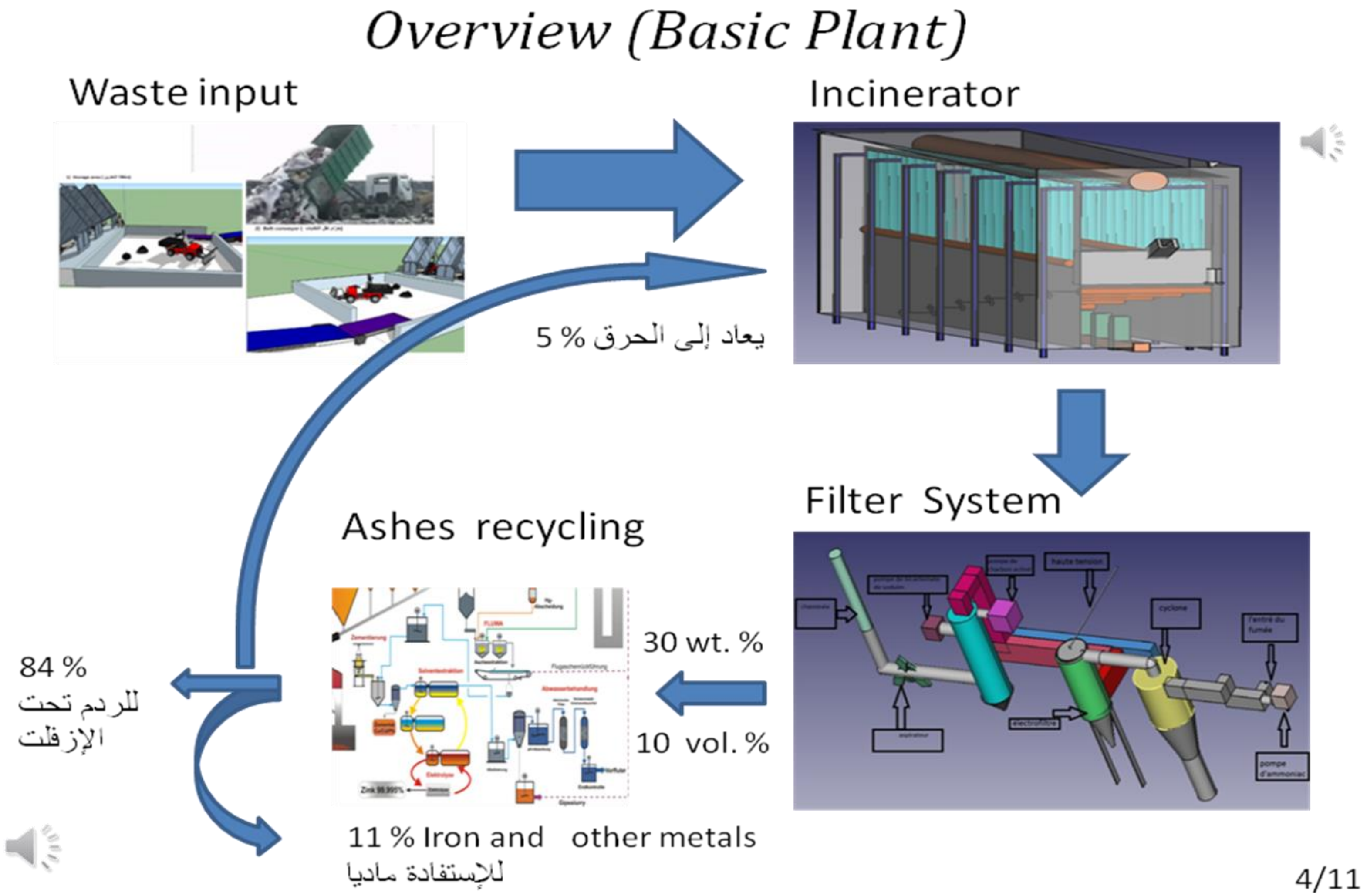
nlaprasnhache
1-5-2017.FCStd

1.4 Option 3



Overview (Basic Plant)

Waste input

Incinerator

5 % يعاد إلى الحرق

Filter System

Ashes recycling

30 wt. %

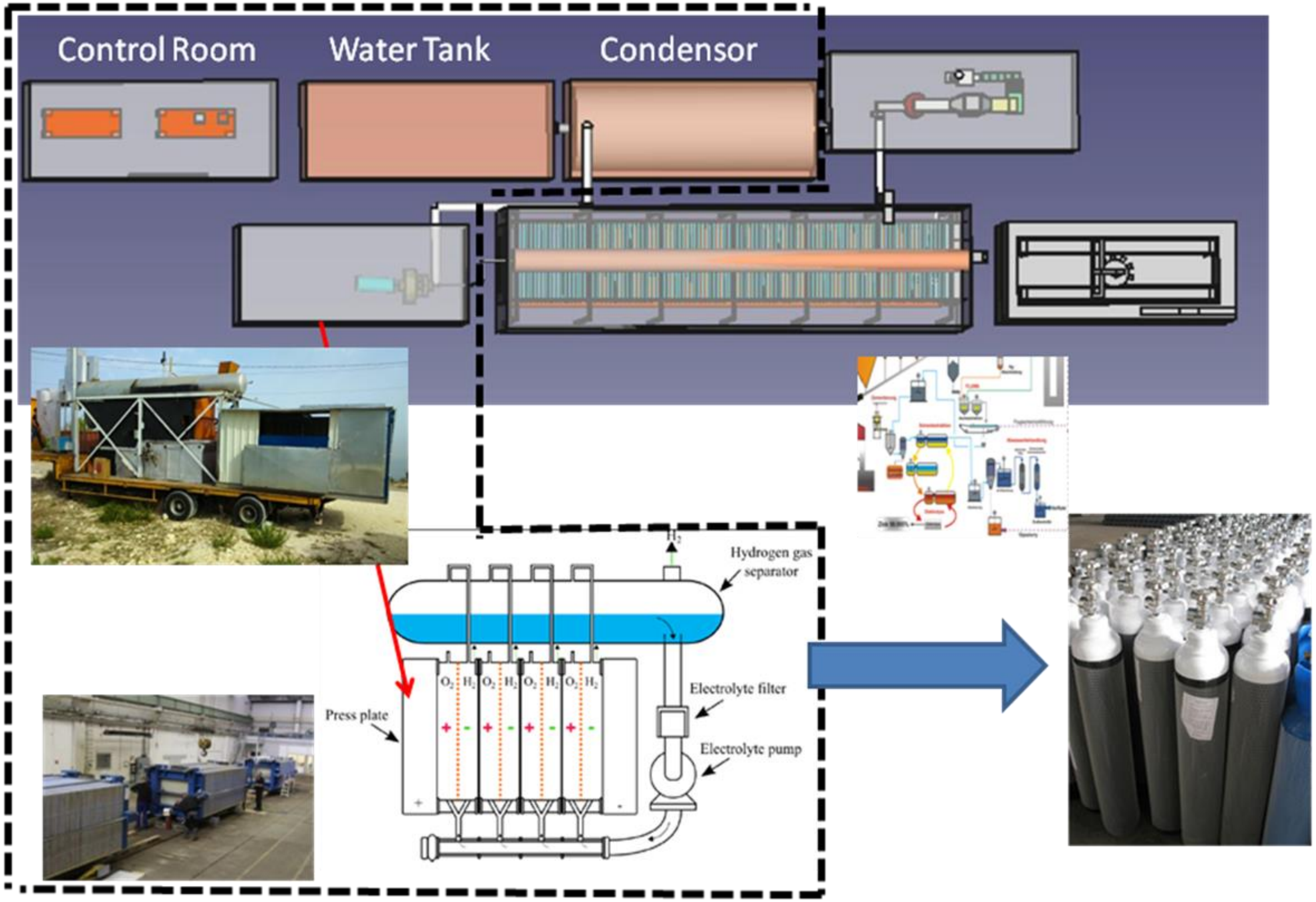
10 vol. %

84 %
للردم تحت
الإزفلت

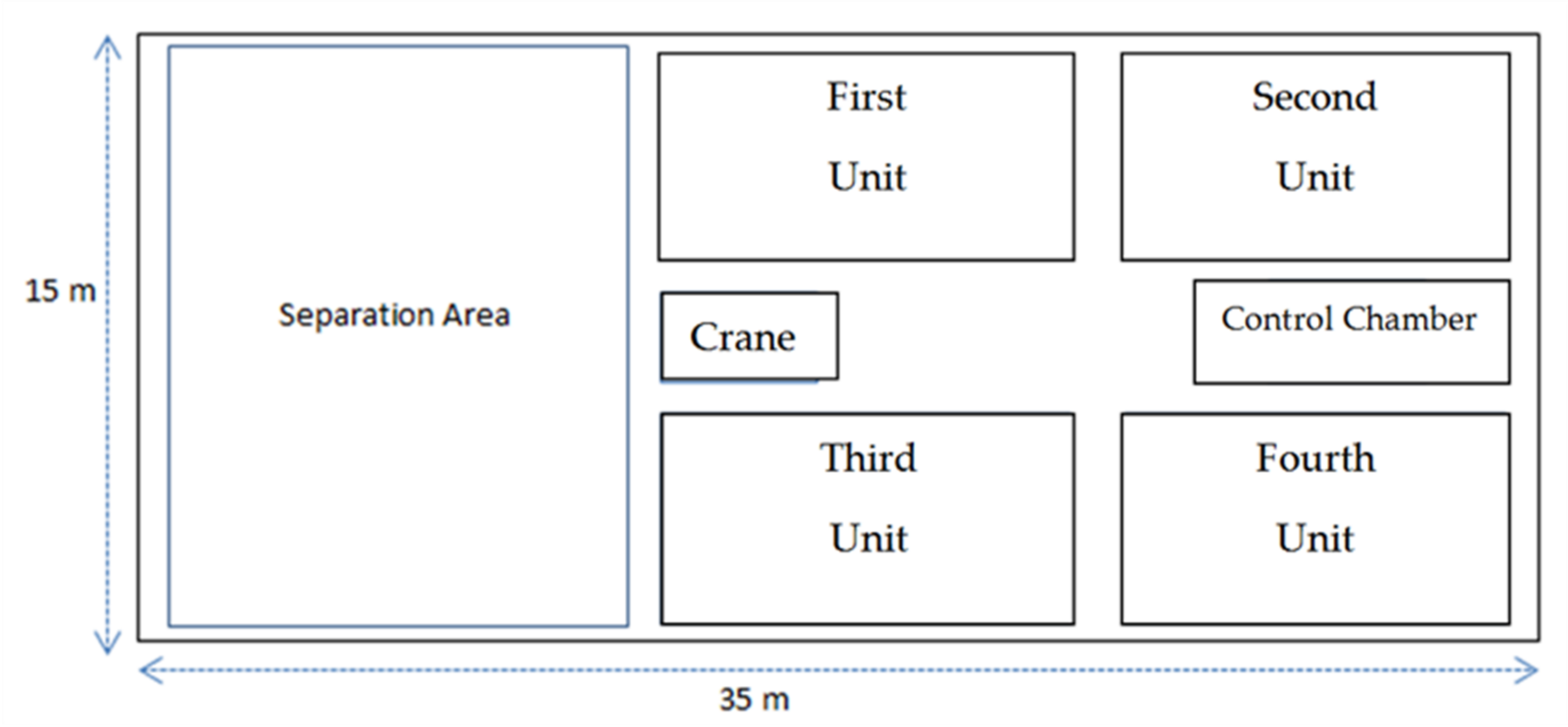
11 % Iron and other metals
للإستفادة ماديا

4/11

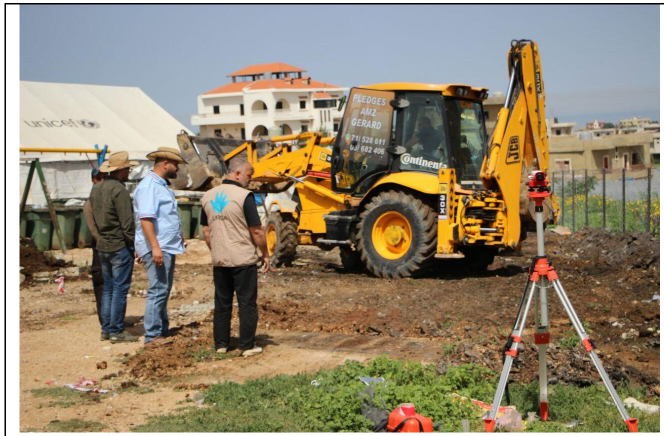
Overview (Optional Components)



مساحة الأرض المطلوبة



1.5 At refugees camp in Rayhaniyye (March - Nov 2018)[1]



Preparation of ground

Visit with major of Mhammra

Visit at 10.06.18

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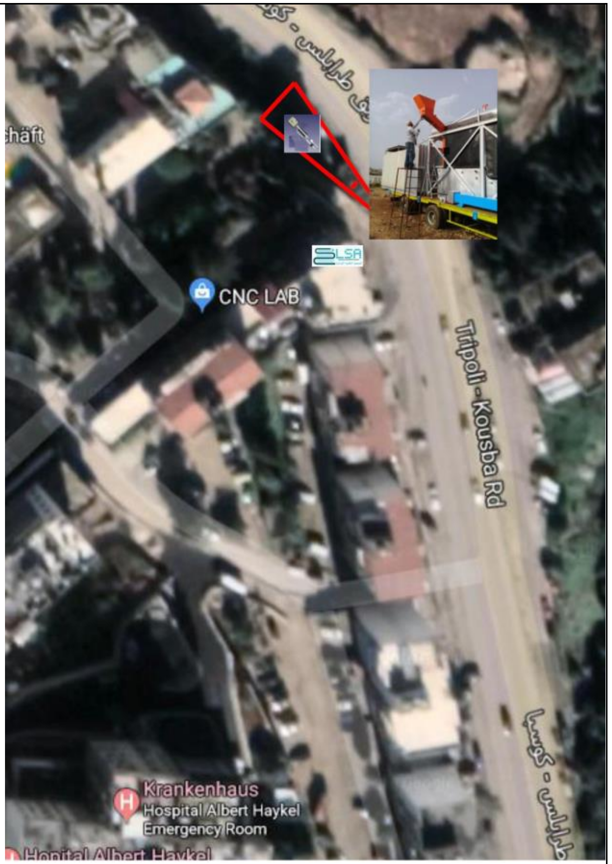
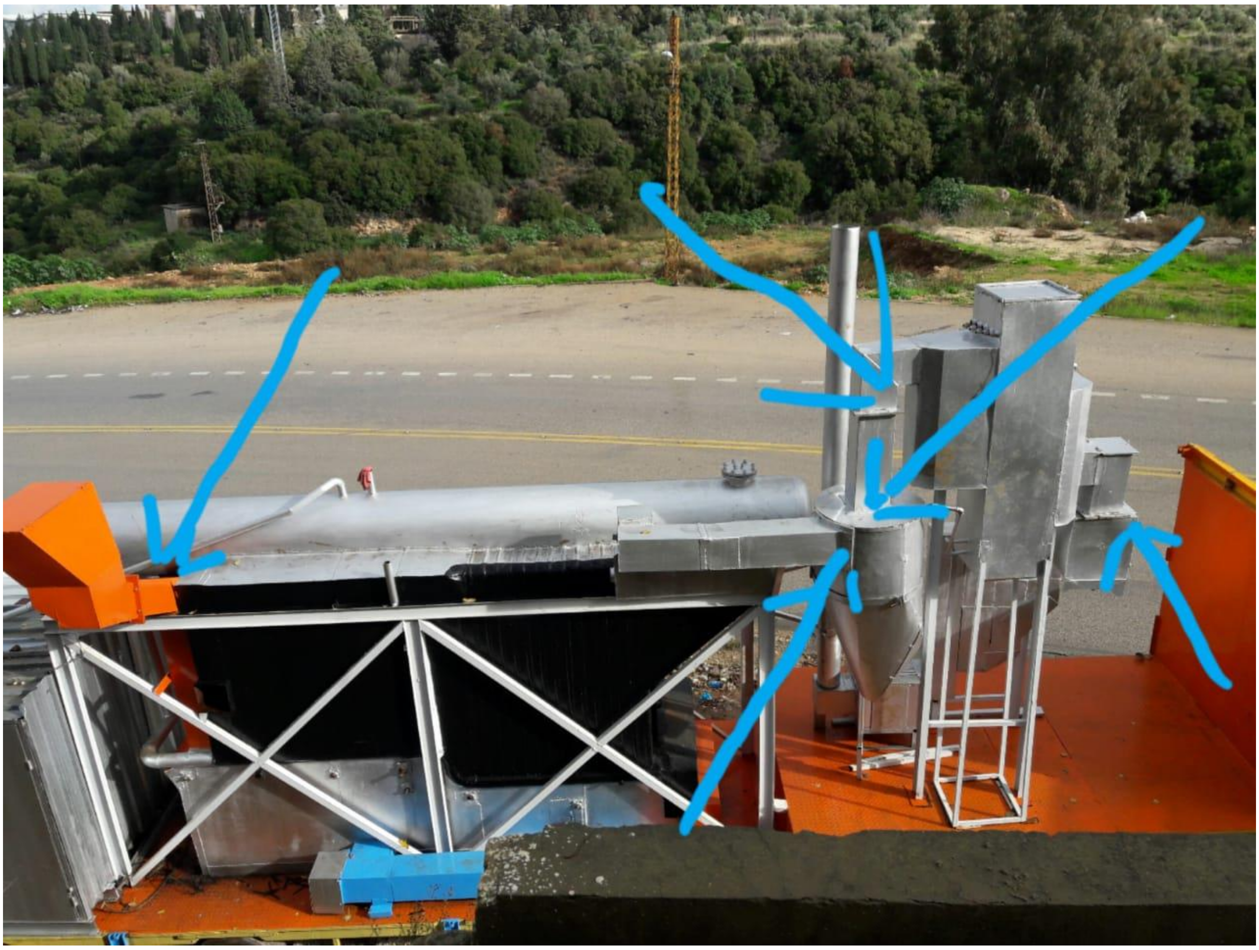
[1] For more details see [EIARayhaniyyeCamp2018]

1.6 Actual Place at Ras Masqa (since November 2018)

	
	الموقع الجغرافي للمحطة في راس مسقا – الكورة

1.6.1 صورة عامة للفلانشات



وضعت هذه الفلانشات من أجل تسهيل عملية تفكيك و تركيب الداخون و المحرقة و الفلاتر التي توجد داخل الداخون.

يتطلب تفكيك هذه الاجزاء، لانها عالية مما يعيق عملية نقل المحطة تحت الجسور على الاتوستراد و أشرطة الكهرباء.

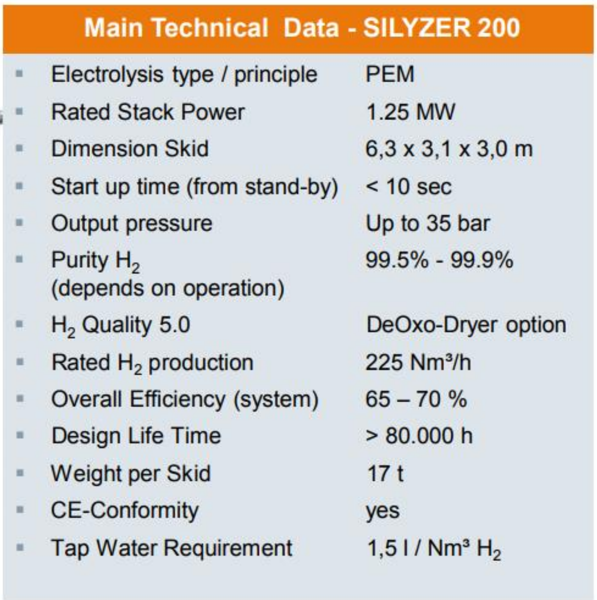
1.6.2 صور الفلانشات تفصيلية

فلانشات للداخون

فلانشات للمحرقة

2 اساسيات (Basics)

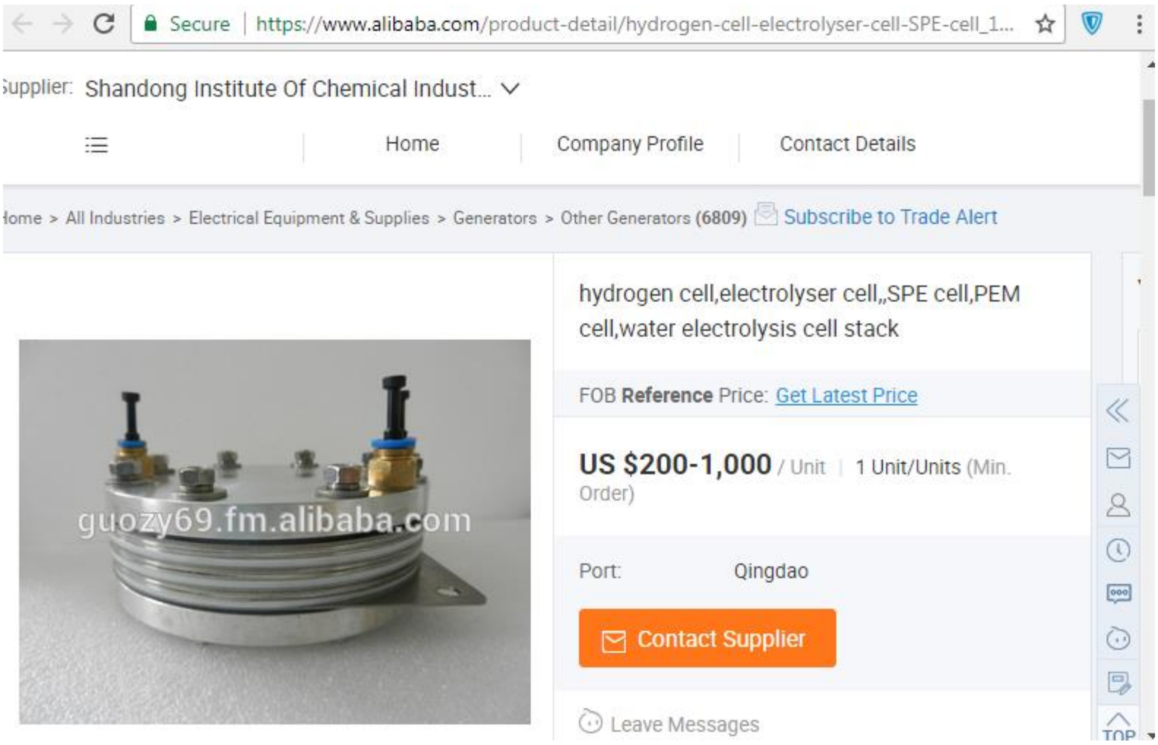
2.1 PEM Electrolysis machine



Main Technical Data - SILYZER 200

Electrolysis type / principle	PEM
Rated Stack Power	1.25 MW
Dimension Skid	6,3 x 3,1 x 3,0 m
Start up time (from stand-by)	< 10 sec
Output pressure	Up to 35 bar
Purity H_2 (depends on operation)	99.5% - 99.9%
H_2 Quality 5.0	DeOxo-Dryer option
Rated H_2 production	225 Nm³/h
Overall Efficiency (system)	65 – 70 %
Design Life Time	> 80.000 h
Weight per Skid	17 t
CE-Conformity	yes
Tap Water Requirement	1,5 l / Nm³ H_2

2.2 PEM Electrolysis cost



Secure | https://www.alibaba.com/product-detail/hydrogen-cell-electrolyser-cell-SPE-cell_1...

Supplier: Shandong Institute Of Chemical Indust...

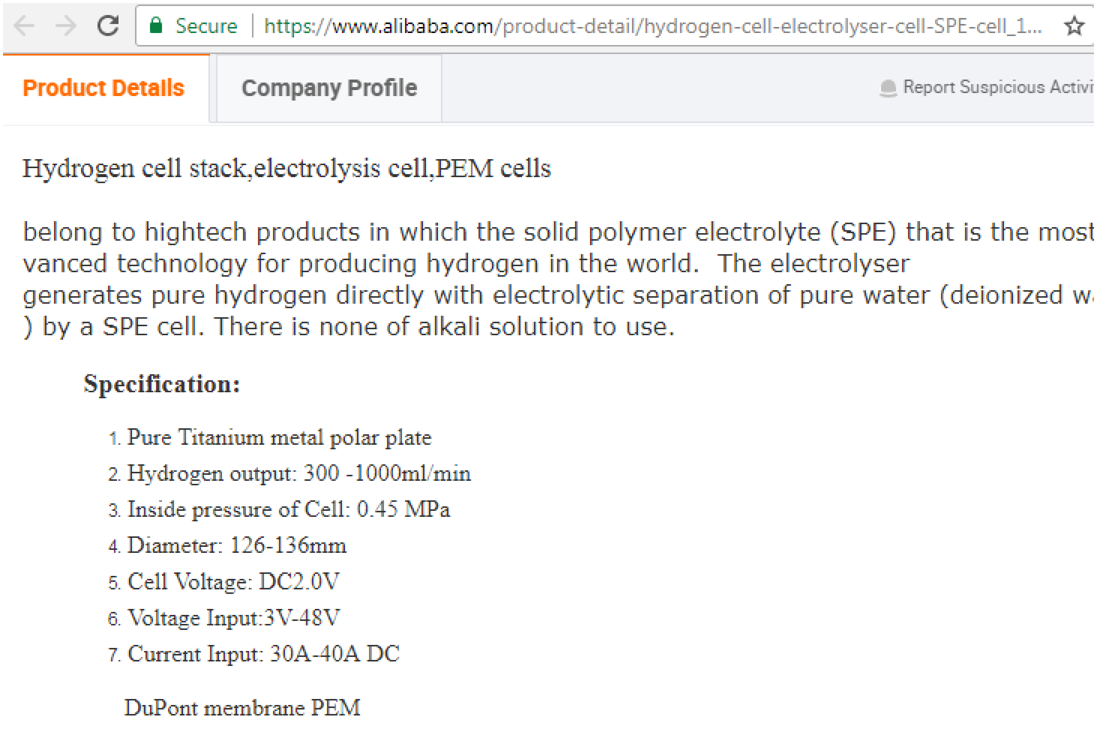
Home > All Industries > Electrical Equipment & Supplies > Generators > Other Generators (6809) Subscribe to Trade Alert

hydrogen cell,electrolyser cell,,SPE cell,PEM cell,water electrolysis cell stack

FOB **Reference** Price: Get Latest Price

US $200-1,000 / Unit | 1 Unit/Units (Min. Order)

Port: Qingdao



Hydrogen cell stack,electrolysis cell,PEM cells

belong to hightech products in which the solid polymer electrolyte (SPE) that is the most
vanced technology for producing hydrogen in the world. The electrolyser
generates pure hydrogen directly with electrolytic separation of pure water (deionized w
) by a SPE cell. There is none of alkali solution to use.

Specification:

1. Pure Titanium metal polar plate
2. Hydrogen output: 300 -1000ml/min
3. Inside pressure of Cell: 0.45 MPa
4. Diameter: 126-136mm
5. Cell Voltage: DC2.0V
6. Voltage Input:3V-48V
7. Current Input: 30A-40A DC

DuPont membrane PEM

https://www.alibaba.com/product-detail/hydrogen-cell-electrolyser-cell-SPE-cell_11262735.html?spm=a2700.7724838.2017115.11.1e94b09aky2NnV (Price 200 - 1000 $)

2.3 Raleigh equation

2.3.1 The Rayleigh Equation

The Rayleigh Equation is useful in the analysis of simple distillation, as it shows **how the concentration and quantity are related.**

As the process is **unsteady state** in nature, the derivation is based on a differential approach to changes in concentration with time. The equation to be derived (known as the Rayleigh Equation) shows the relationship between **total moles remaining in the still** and the **mole fraction of the more volatile component in the still.**

[Similar equation can be obtained for the relationship between the total moles of distillate and the mole fraction of the more volatile component in the condensate receiver]

Material Balance for the still: see the Figure below

L_1 = initial moles of liquid originally in still

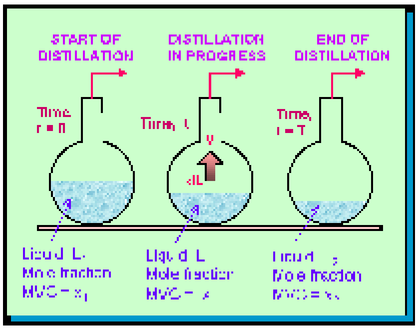
L_2 = final moles of liquid remained in still

x_1 = initial liquid composition in still (mole fraction of A)

x_2 = final liquid composition in still (mole fraction A)

At any time t, the amount of liquid in the still is L, with mole fraction of A in the liquid being x.

After a small differential time (t + dt) , a small amount of vapour dL is produced, and the composition of A in the vapour is y (mole fraction). The vapour is assumed to be **in equilibrium** with the residue liquid.The amount of liquid in the still is thus reduced from L to (L - dL), while the liquid composition changed from x to (x - dx). See the Figure below:



Performing a material balance on A:

Initial amount in still = Amount left in still + Amount vaporized

We have,

$$xL = (x - dx)\,(L - dL) + y\,dL$$

$$xL = xL - x\,dL - L\,dx + dx\,dL + y\,dL$$

Neglecting the term dx dL, the equation reduces to:

L dx = y dL - x dL

Re-arranging gives the following:

$$\left(\frac{dL}{L}\right) = \frac{dx}{(y-x)}$$

Integrating from L_1 to L_2, and from x_1 to x_2, we obtain the **Rayleigh Equation:**

$$\ln\left[\frac{L_1}{L_2}\right] = \int_{x_2}^{x_1} \frac{1}{(y-x)}\,dx$$

2.4 Metal reactions with acids

2.4.1 Reaktion von Metallen mit Salpetersäure[2]

1.

Versuchsaufbau: Proben von Kupfer, Aluminium und Zink, Zugabe von Salpetersäure.

2.

Nur Kupfer zeigt eine deutliche Reaktion

1.Bild-Versuchsaufbau: Es werden gleichzeitig Proben der Metalle Kupfer und Aluminium mit konzentrierter Salpetersäure und von Zink mit verd. Salpetersäure versetzt. Direkt nach der Zugabe findet im Fall von Zink und Aluminium noch keine Reaktion statt, Kupfer reagiert dagegen sofort, es kommt zur Bildung von braunem NO_2 nach

$$Cu + 2\,HNO_3 + 2\,H^+ \longrightarrow Cu^{2+} + 2\,NO_2 + 2\,H_2O$$

2.Bild: Keine Reaktion bei Aluminium, kaum sichtbare Reaktion bei Zink, weiterhin heftige Reaktion bei Kupfer.

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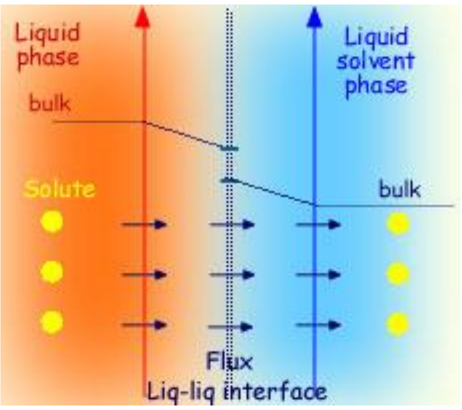
[2] http://www2.uni-siegen.de/~pci/versuche/v44-24-2.html

2.5 Liquid-Liquid separation

2.5.1 Definitions and aims[3]

The liquid-liquid extraction or simply liquid extraction is a process where one or more solutes are removed from a liquid phase, called diluent, and transferred into a second liquid phase, called solvent, by simple contact of the two liquids.

The two liquids must be either immiscible or partially miscible so that only the solute, which has a greater solubility in the solvent phase than in the diluent, separates from this and moves into the solvent.



Extraction is a common laboratory and industrial unit operation and since it does not involve any evaporation process, can be carried out also at low temperature, thus making this process so convenient also for high temperature-sensitive products.

In the following sections we will focus on the case of partially miscibility between diluent and solvent, hence on extraction with ternary systems.

In the case of total immiscibility, the extraction problem becomes similar to the absorption and stripping type of problem. In this case the McCabe-Thiele graphical method, developed for absorption and stripping, can be easily applied also to design extraction processes.

2.5.2 Process description

The purpose is to recover a certain substance (the solute) at high purity by the use of a high selective solvent.

In the extraction unit, a solute (yellow) is separated from the feed (orange) and moves into the solvent (blue). In the further step, in the solvent recovery unit, the solute is finally separated from the solvent, e.g. by distillation or by other unit operations, and obtained high pure.

Let us exploit, now, the extraction unit (please click on it to see more).

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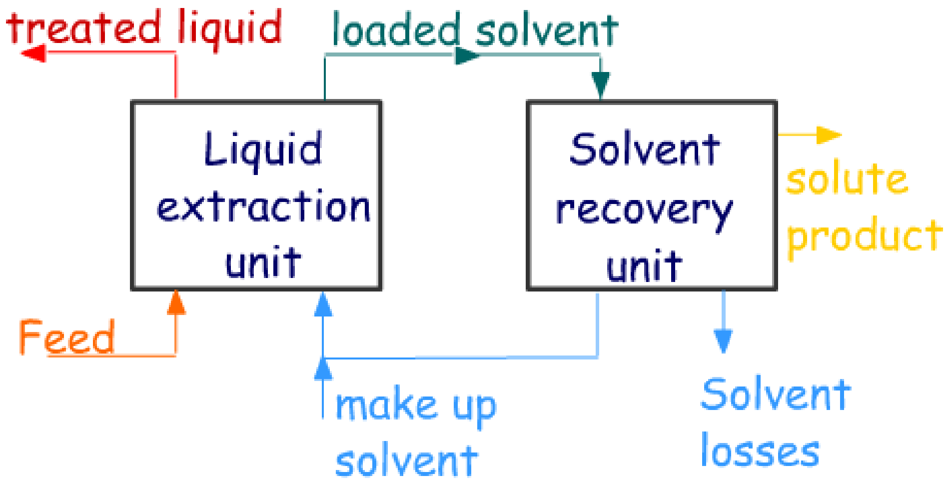
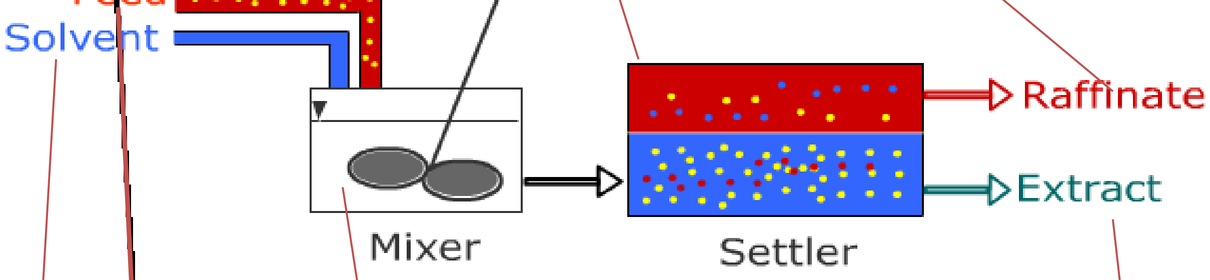
[3] http://www.hyper-tvt.ethz.ch/extraction-definitions.php



2.5.2.1 Liquid extraction unit:

The settler allows for the mechanical separation of the two phases due to their difference in density, which is the driving force for the separation. This is a critical step since the density difference is never so big (both are liquids).

The raffinate is the product of the extraction rich in the diluent phase. It contains also trace of solute and of solvent since these are partially miscible.



A liquid mixture containing the carrier solvent, called diluent, and the solute is fed to the mixer unit

The solvent is generally pure and high selective for the solute (high solubility)

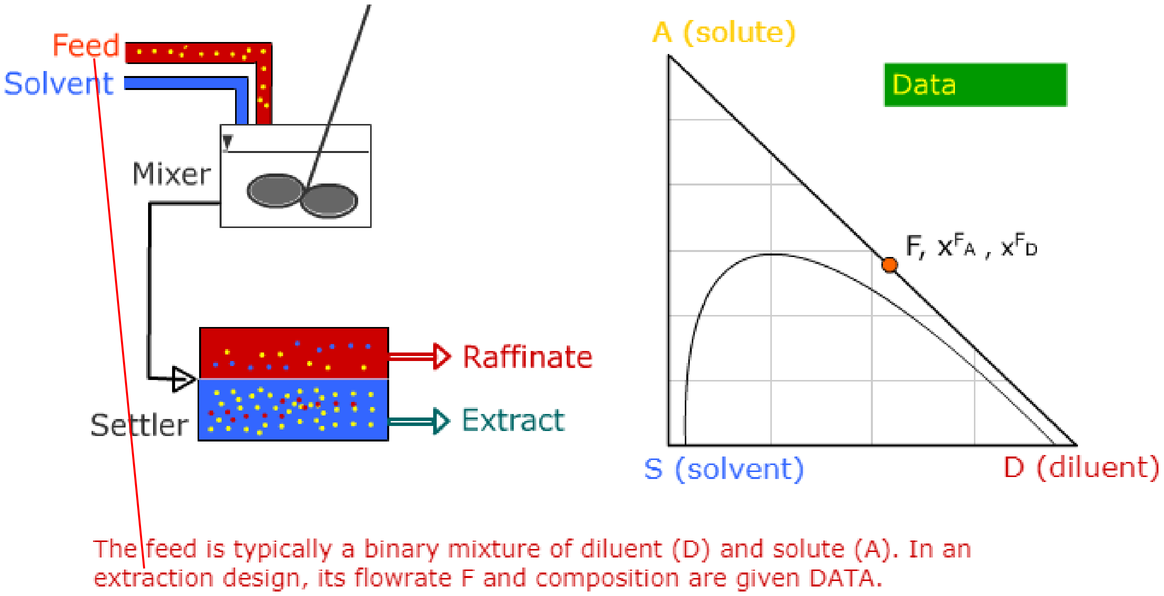
The feed and the solvent phases come in contact and the mass transfer takes place. During this phase (extraction) the solute moves from the feed phase to the solvent. We assume that the ideal equilibrium conditions are reached.

The extract is the product rich in the solvent and solute. This must be further treated (e.g. with distillation) to recover the solute.

2.6 Single stage: problem definition

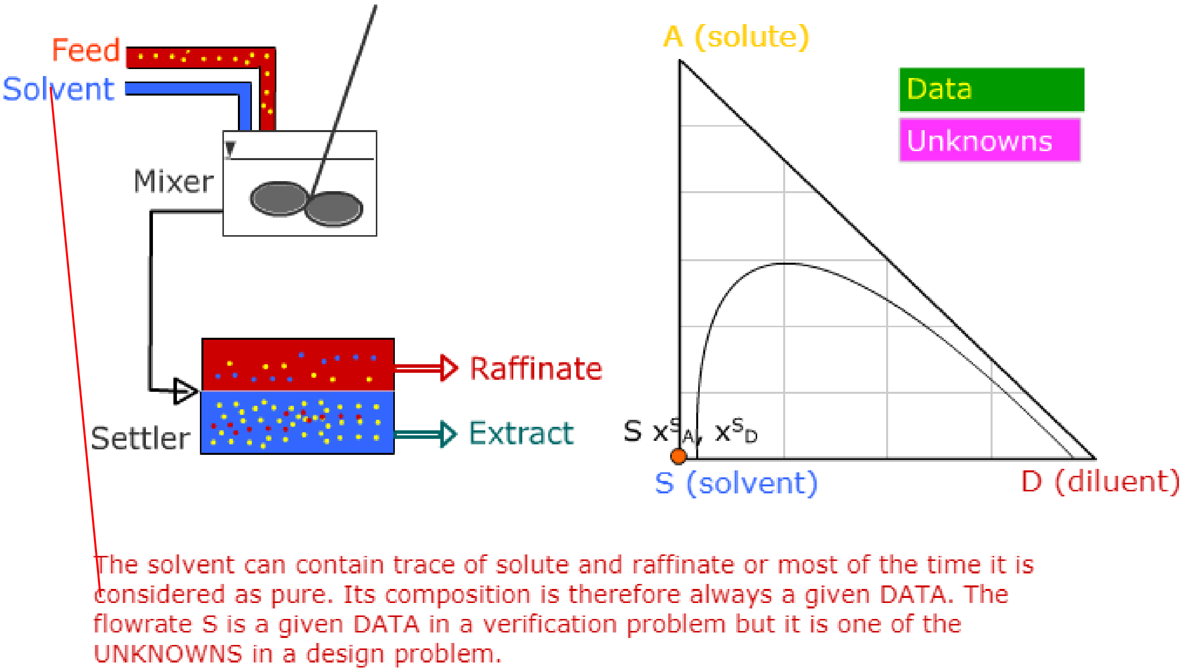
The most simple extraction process can be carried out with a simple mixer and a settler. This is called single equilibrium stage since the feed and the solvent come in contact in only one mixer (=stage). Ideal equilibrium condition is assumed.

2.6.1 Feed



The feed is typically a binary mixture of diluent (D) and solute (A). In an extraction design, its flowrate F and composition are given DATA.

2.6.2 Solvent

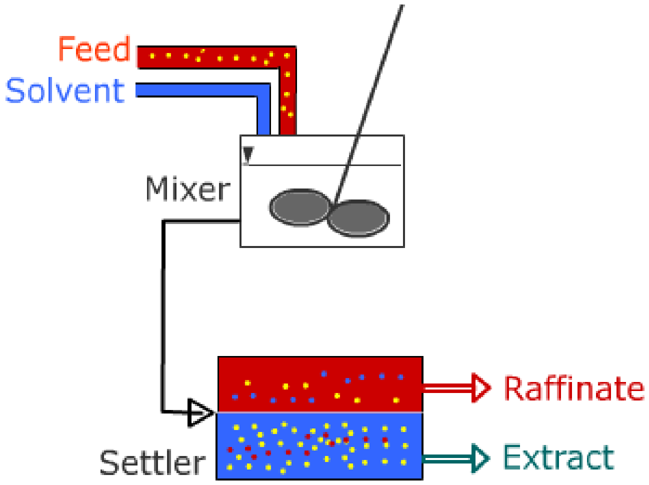


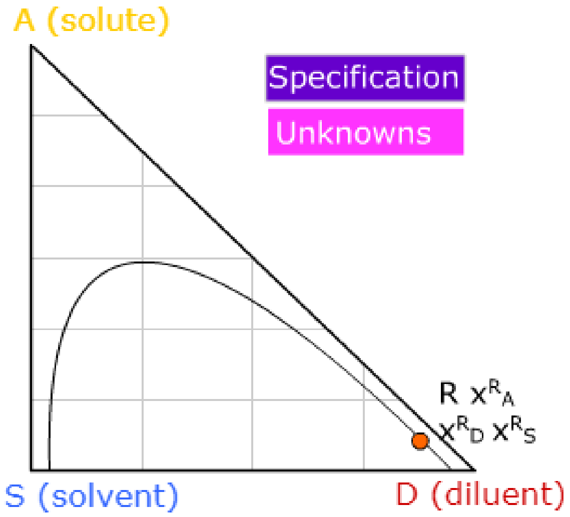
The solvent can contain trace of solute and raffinate or most of the time it is considered as pure. Its composition is therefore always a given DATA. The flowrate S is a given DATA in a verification problem but it is one of the UNKNOWNS in a design problem.

The mixer is the equilibrium stage. The feed and the solvent exchange solute until the equilibrium is reached.

The settler allows for the mechanical separation of the two phases (extract and raffinate), which have reached the equilibrium in the mixer. No further mass transfer or thermodynamics phenomena take place in the settler.

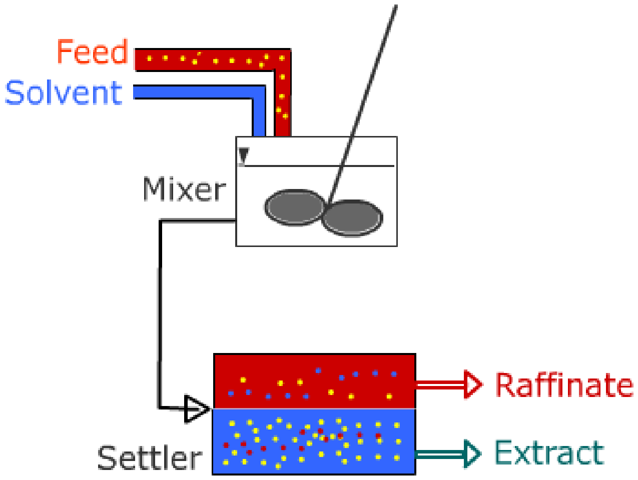
2.6.3 Raffinate:

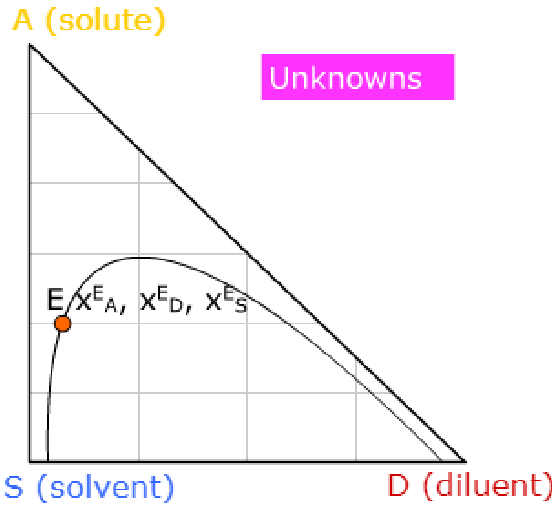




The final content of solute in the raffinate is the given SPECIFICATION of the extraction task. The raffinate comes out from an equilibrium stage therefore its composition is on the solubility envelope. Its flowrate R and its content of solvent and diluent are UNKNOWNS.

2.6.4 Extract





The extract composition and flowrate E are some of the UNKNOWNS of the extraction task. The composition must be a point of the solubility envelope and correlated with the raffinate composition with a tie-line (equilibrium condition).

2.7 Single stage: process design

In the case of a simple mixer (one equilibrium stage), the design consists in sizing the flow rate of the solvent which must be used to obtain the required extract composition and in calculating the obtained extract and raffinate flow rate.

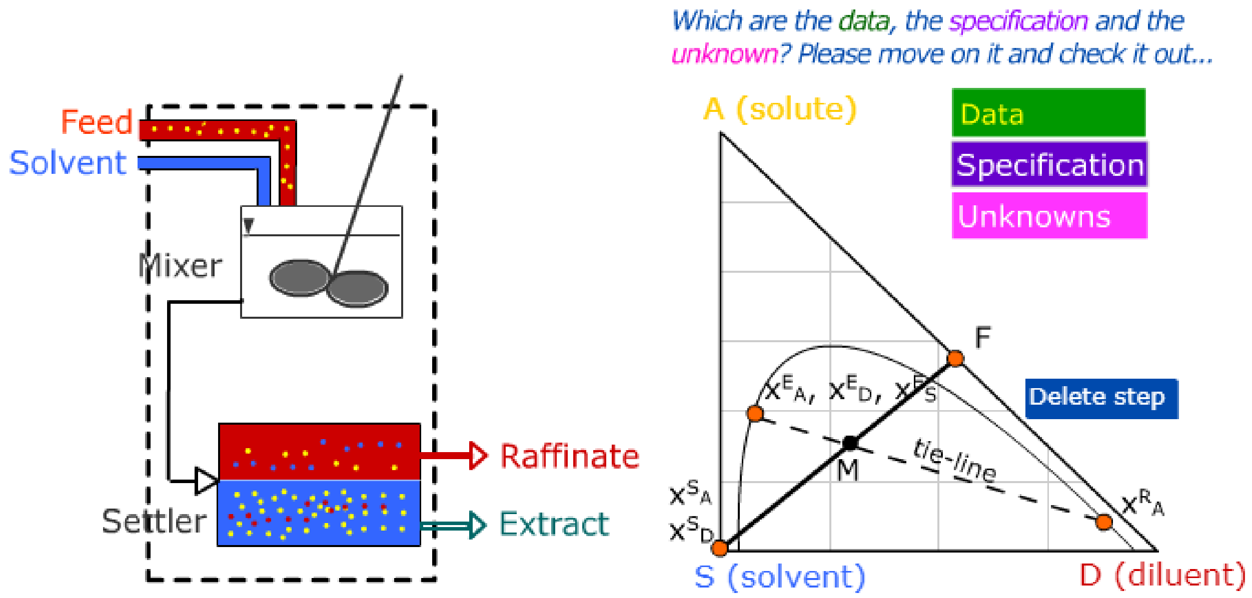
In order to do this, typically a graphical method is used as shown in the following procedure. Please click on the steps here below to run the animation.

Please, note that for the seek of simplicity the **solvent** is considered to be **pure**. However, in reality, most likely the solvent comes from a regeneration step and therefore contains still trace of solute (see extraction unit configuration - paragraph 1.2)

- **Step1.** Tie-line through the raffinate composition --> Extract composition determination
- **Step2.** Overall mass balance and lever-arm rule--> mixing point M identification
- **Step3.** Application of the lever-arm rule to calculate the flow rates S, R, E

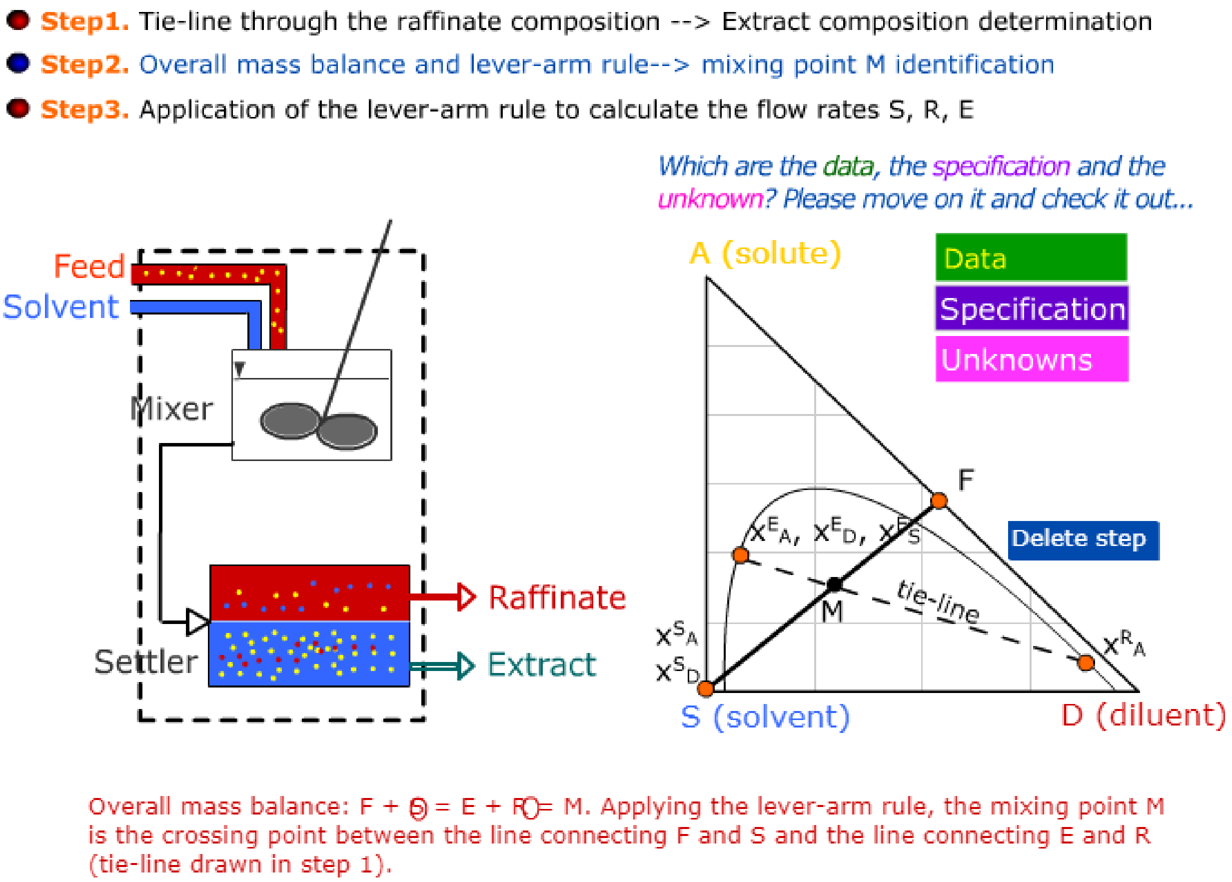
2.7.1 Step 1

- **Step1.** Tie-line through the raffinate composition --> Extract composition determination
- **Step2.** Overall mass balance and lever-arm rule--> mixing point M identification
- **Step3.** Application of the lever-arm rule to calculate the flow rates S, R, E



The tie-line (equilibrium line) through the given raffinate specification is drawn and the extract composition can be read on the diagram. The raffinate and the extract are at equilibrium since they come from the same equilibrium stage (mixer).

2.7.2 Step 2



- **Step1.** Tie-line through the raffinate composition --> Extract composition determination
- **Step2.** Overall mass balance and lever-arm rule--> mixing point M identification
- **Step3.** Application of the lever-arm rule to calculate the flow rates S, R, E

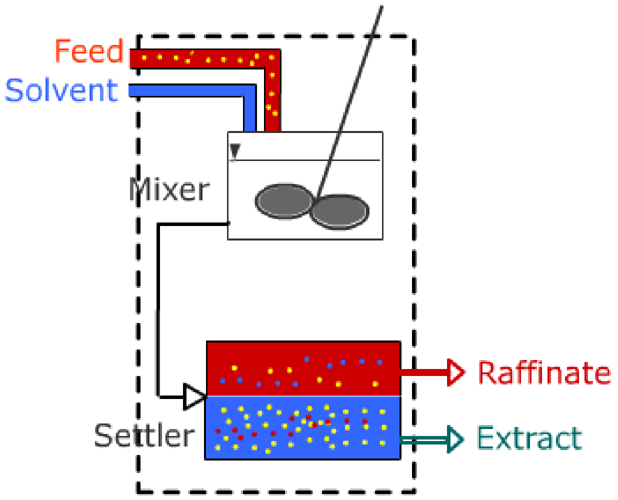
Which are the data, the specification and the unknown? Please move on it and check it out...

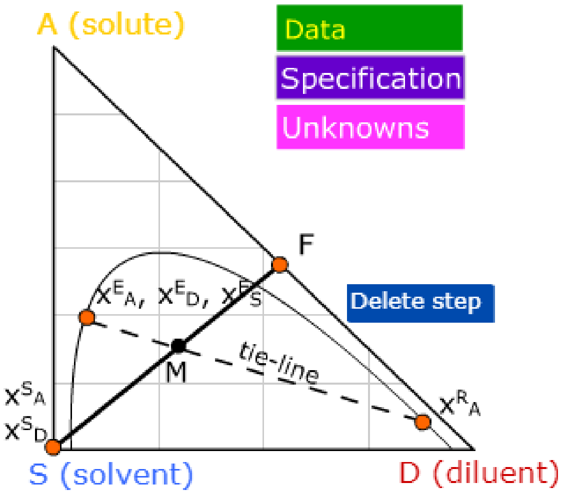
Overall mass balance: F + S = E + R = M. Applying the lever-arm rule, the mixing point M is the crossing point between the line connecting F and S and the line connecting E and R (tie-line drawn in step 1).

2.7.3 Step 3

- **Step1.** Tie-line through the raffinate composition --> Extract composition determination
- **Step2.** Overall mass balance and lever-arm rule--> mixing point M identification
- **Step3.** Application of the lever-arm rule to calculate the flow rates S, R, E

Which are the data, the specification and the unknown? Please move on it and check it out...





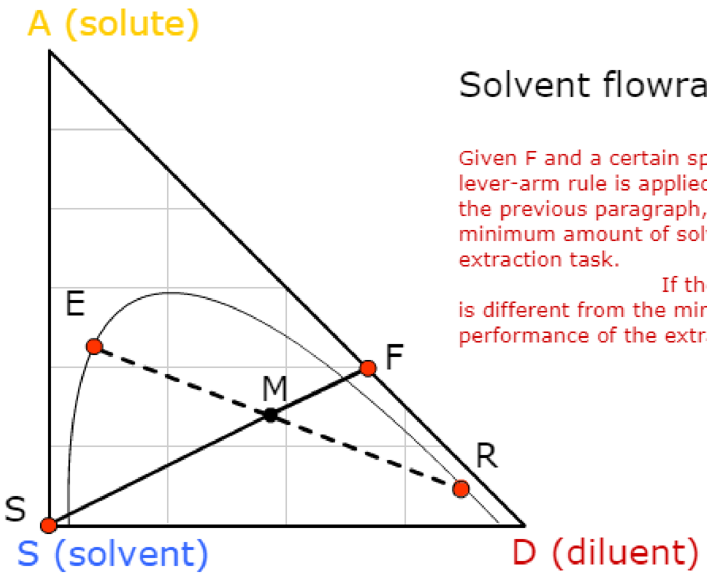
Finally the lever-arm rule is applied to determine respectively the flowrate S, R, and E.

$$\frac{\overline{MF}}{\overline{MS}} = \frac{S}{F} \qquad \frac{\overline{ME}}{\overline{ER}} = \frac{R}{F \oplus S} \qquad \frac{\overline{MR}}{\overline{ME}} = \frac{E}{R}$$

2.8 Single stage: solvent range

In the following animation we would like to use the graphical method to show how the change in the solvent flow rate S impacts on the liquid extraction performance in the case of a **simple mixer** (single equilibrium stage).

Please **click once** on the "up" arrow or on the "down" arrow to run the animation. The animation is only **qualitative**.

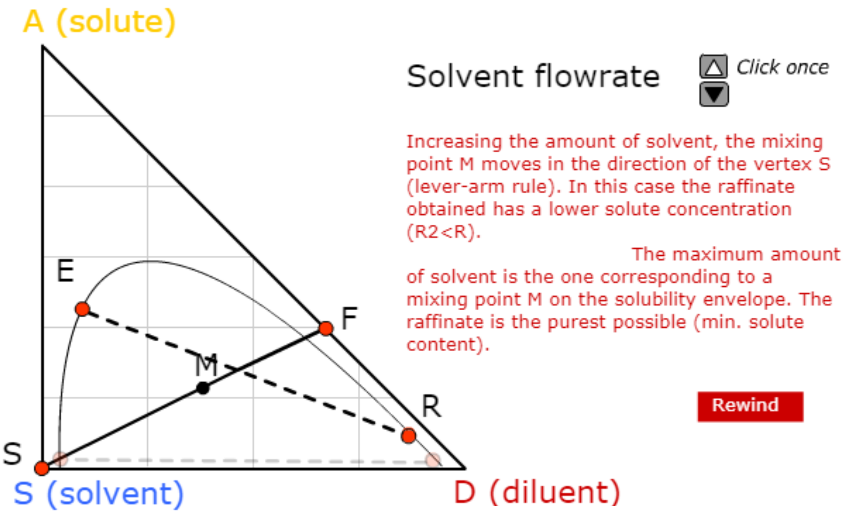


Solvent flowrate ▲ ▼

Given F and a certain specification on R, the lever-arm rule is applied, as shown already in the previous paragraph, to determine the minimum amount of solvent S to carry out the extraction task.

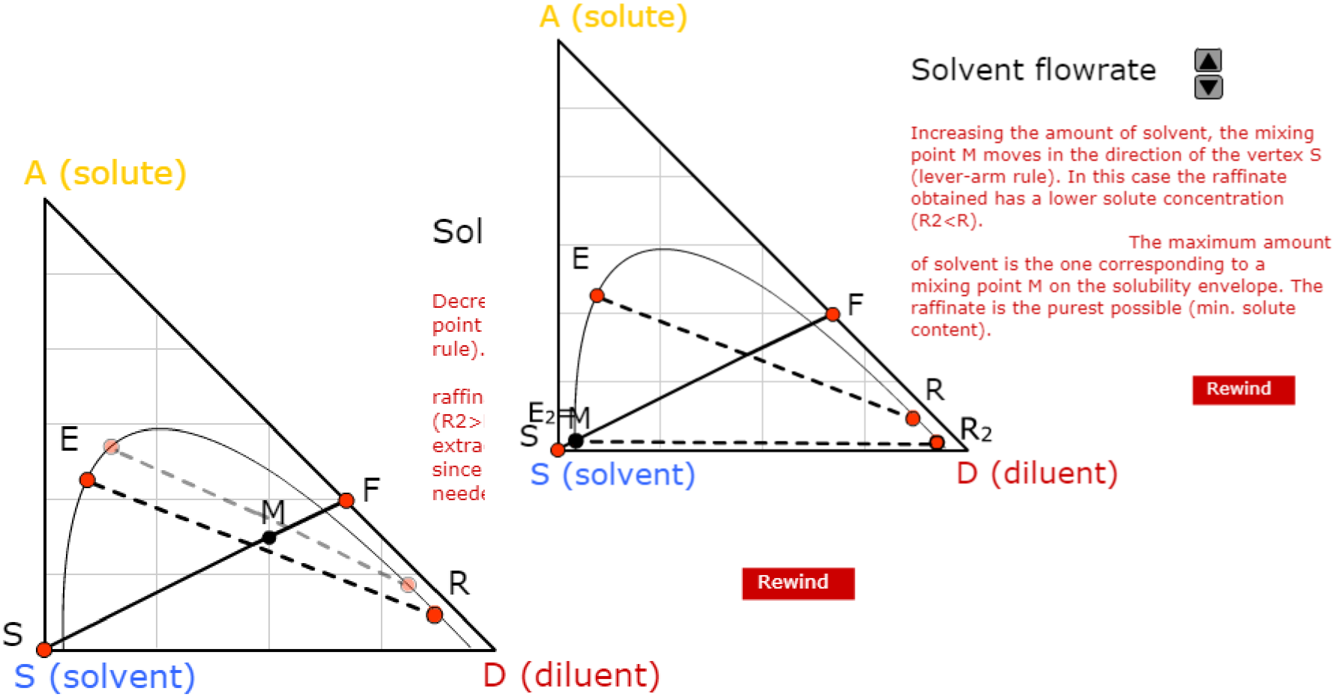
If the amount of solvent S is different from the minimum one the performance of the extraction unit changes.

Rewind



Increasing the amount of solvent, the mixing point M moves in the direction of the vertex S (lever-arm rule). In this case the raffinate obtained has a lower solute concentration (R2<R).

The maximum amount of solvent is the one corresponding to a mixing point M on the solubility envelope. The raffinate is the purest possible (min. solute content).



Increasing the amount of solvent, the mixing point M moves in the direction of the vertex S (lever-arm rule). In this case the raffinate obtained has a lower solute concentration (R2<R).

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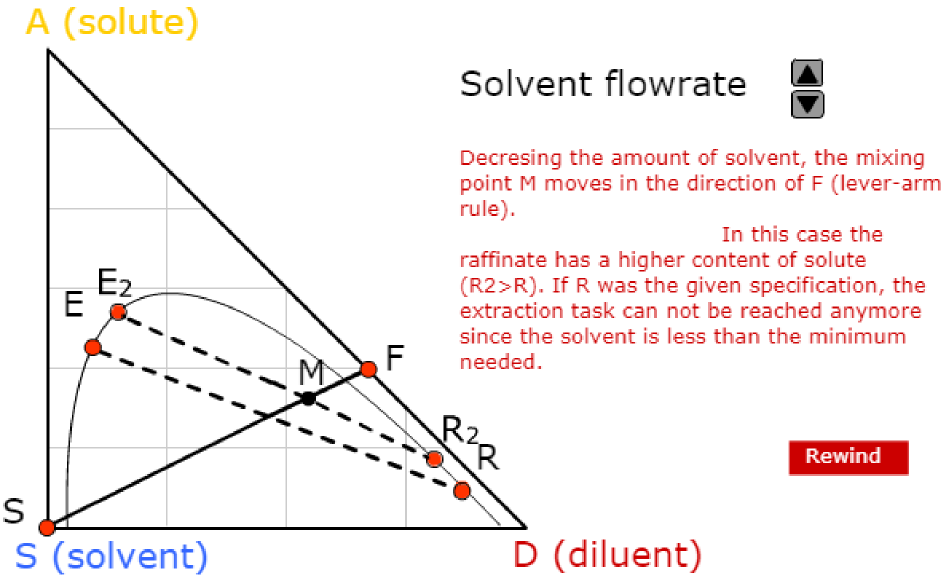


Decresing the amount of solvent, the mixing point M moves in the direction of F (lever-arm rule).

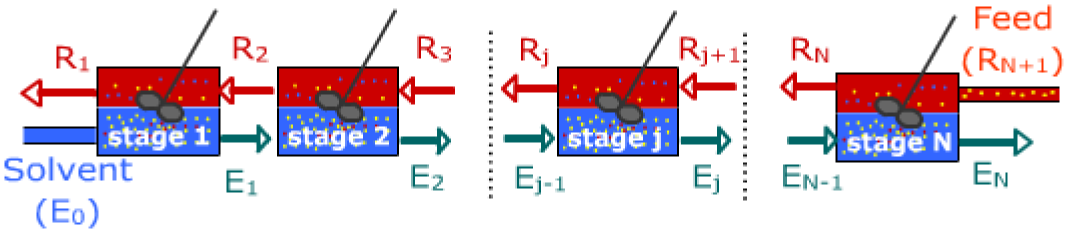
In this case the raffinate has a higher content of solute (R2>R). If R was the given specification, the extraction task can not be reached anymore since the solvent is less than the minimum needed.

2.9 Counter-current: column configuration

The best configuration for a cascade of mixers and settlers (= single stage) is the so-called **counter-current configuration**. This layout allow for still better separation for the same number of stages compared to a cross-current configuration.

The cascade of stages is finally arranged in a column, called extraction column. Please, refer to the contactors section to learn more on this topic.

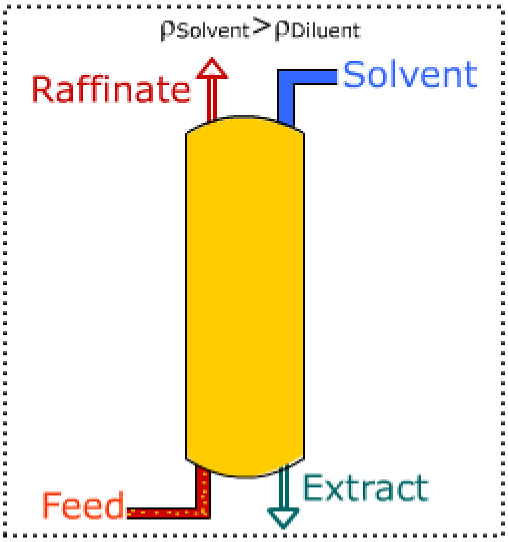
Please move on the schema here below to run the animation.



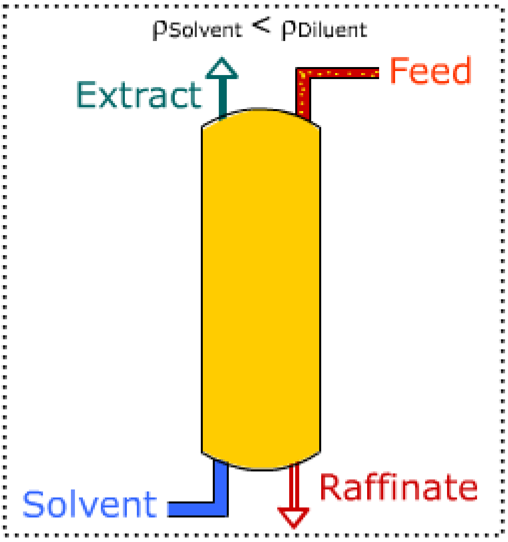
In the counter-current configuration a cascade of N stages (mixer+settler) is arranged like in the figure.

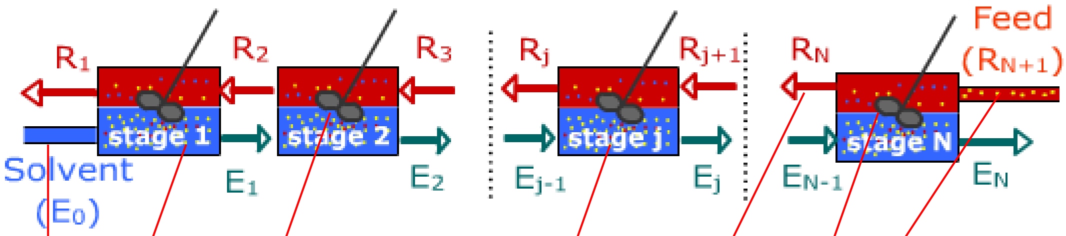
Ideal equilibrium conditions are assumed within each stage.

● column configuration 1



● column configuration 2





The feed is conventionally fed at the stage N in counter-current with the solvent. The feed comes in contact with the extract stream, which will leave the cascade of stage as a product.

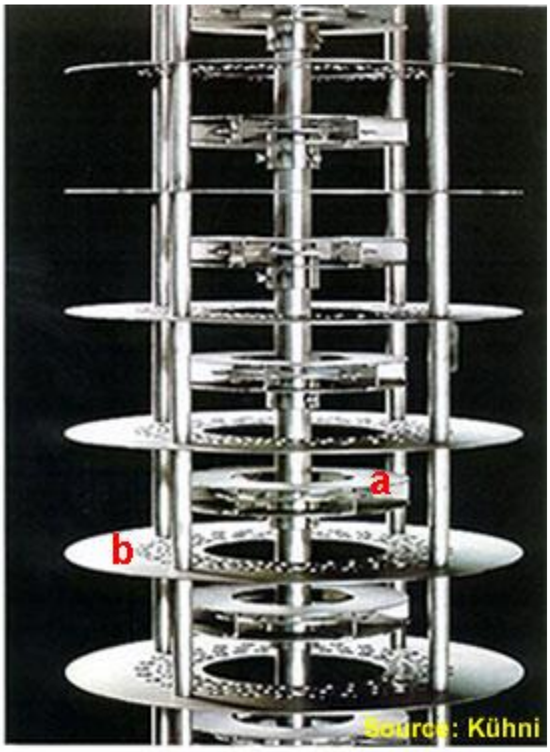
Ideal equilibrium conditions are assumed within each stage. Therefore the extract and the raffinate streams coming out from the same stage are at equilibrium. For convention these streams take the index name of the stage (Rj, Ej come out of stage j).

The raffinate stream is fed to the next stage in counter-current with the extract. For convention the concentration in the raffinate phase is indicated with 'xj' for a stream leaving stage j and 'xj+1' for a stream entering stage j.

The fresh solvent is fed at stage 1 of the cascade of stages. It comes in contact with the raffinate stream flowing counter-currently with respect to it.

2.10 Liquid-liquid extraction columns

The video illustrates the operation of a mechanically agitated, counter-current liquid-liquid extraction column, which employs a rotating agitator driven by an axial shaft.

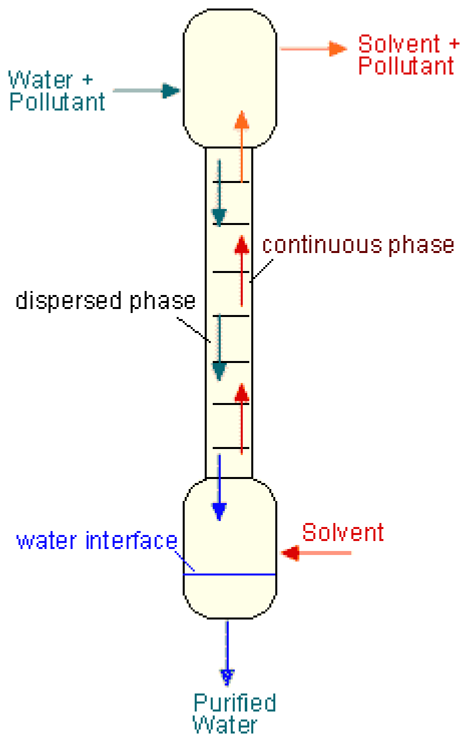


There are several types of such columns that are commercially available, e.g. the Scheibel, Oldshue, Rushton, K?hni columns and the rotating-disk contactors.

In all cases, the agitation **enhances mass transfer** by promoting the dispersion of one phase into the other and the **creation of interfacial surface**. The agitators create mixing zones, alternating with settling zones along the column.

The difference among the various commercial columns lies in the **design** of the agitation elements (indicated with **a** in the figure) and the stator disks (indicated with **b** in the figure).

The particular column presented in the video is a pilot K?hni column. The column is installed for separation development and customers tests at the Basel headquaters of the Swiss company K?hni, which has been successful in developing and commercialising this process equipment for a fews decades.



The **aim** of the extraction process is to purify an aqueous stream (**heavy, dispersed phase**) by extracting a polluting solute with a water-immiscible organic solvent (**light, continuous phase**). The pollutant has a larger affinity for the organic than for the aqueous phase, hence it is transferred from the latter to the former phase along the column.

2.11 Practica in Process Engineering: Liquid-Liquid Extraction[4]

Introduction

Extraction is a process in which one or more components are separated selectively from a liquid or solid mixture, the feed (Phase 1), by means of a liquid immiscible solvent (Phase 2). The transfer of the components from the feed to the solvent is controlled by the solubility behavior of each component in the corresponding phase. Two phases result from the extraction step: one enriched (EXTRACT Phase) and the other depleted (RAFFINATE Phase) in the components to be separated, respectively. Afterwards in order to regenerate the solvent, another separation step (e.g. distillation) is finally required. Liquid-liquid extraction is most widely used and will be considered within this laboratory. It is applied e.g. to remove heavy metals or acids from waste water or for the production of aromatic compounds from mixtures of hydrocarbons. Another application is gas-liquid extraction which is also called absorption.

Figure 1 shows the four streams involved in the extraction process with the common nomenclature in the case when component B is separated from the mixture of A and B by means of a solvent C, i.e. $AB + C -> A + CB$. This nomenclature will be kept during the whole theoretical part of this handout.

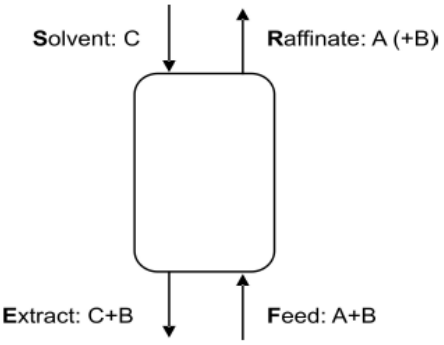


Figure 1: A typical extraction step.

Compared to distillation, extraction processes have the disadvantage that a new component is added to the system. This leads to additional impurities as complete immiscibility does only exist in theory. Furthermore a subsequent separation process is required to regenerate the solvent. However, there are a number of situations in which extraction is advantageous and they are summarized in the following:

- One or more components in the mixture are not thermally stable.
- The components in the mixture have a very high or low boiling point requiring vacuum or cryogenic distillation, which is very energy intensive.
- The boiling points of the components are very close or they form azeotropes.

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[4] https://www.ethz.ch/content/dam/ethz/special-interest/mavt/process-engineering/separation-processes-laboratory-dam/documents/practica%20in%20process%20engineering%202/extraction.pdf

- Two components with very different boiling points have to be separated at the same time.
- The components to be separated (pollutants or valuable products) are only a small fraction of the mixture.

If you have not attended any course about extraction yet, it is highly recommended to have a look at the Hyper-TVT homepage [1], which explains briefly the concept of counter flow extraction columns (Section "Liquid-liquid extraction")!

Theoretical background

The concept of extraction: the one stage extractor

The simplest form of an extractor apparatus has only one stage and the process is performed in two steps. In the first step, the feed is mixed with the solvent to create a high surface area allowing to achieve high mass transfer rates. The mass transfer stops when thermodynamic equilibrium between the two phases is reached. Equilibrium is characterized by an equal temperature, equal pressure and equal chemical potentials in both phases. In the second step the two phases are allowed to separate (settling process). Finally, after decanting one receives the raffinate and the extract. Figure 2 illustrates the concept.

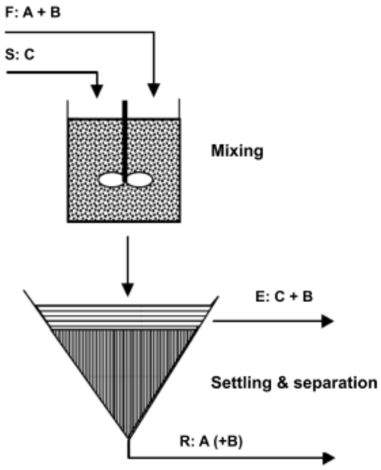


Figure 2: The one-stage extractor.

To allow an optimal extraction process, it is crucial to ensure a good mixing between the solvent and the feed, to have enough contact time between the two phases and to give enough settling time to separate the two phases. Considering this process, a number of requirements for a suitable solvent C can be specified:

- high capacity for component B
- high selectivity for component B
- low solubility in A (and vice versa)

- simple separation between B and C
- considerable difference in the densities compared to A
- low surface tension
- low viscosity
- chemical and thermal stability
- nontoxic
- no or low corrosivity
- low cost

However, in order to obtain the required separation several steps of mixing and phase separation are mostly needed. Therefore, in practical applications multi-stage extractors are usually used. As for many separation processes, a co-, a cross-, or a counter-flow concept can be applied [1]. Some of the important aspects for designing multi-stage extractors are discussed in the following sections.

Multistage exercise and 3-component diagrams

In this exercise, we will discuss how to combine thermodynamic data (represented by a 3-component-diagram) with a mass balance in order to design an extraction process. In our case, we have an aqueous phase (water), an organic phase (toluene) and a component (acetone) which is meant to be extracted. Please note that for educational purpose, the acetone concentration in this exercise is much higher than during your experiments (safety concerns).

3-component-diagrams

Have a look at the diagram (handed out during the experiments):

- Where are the pure components?
- Where is only one phase, where are two phases?
- What is the name of the lines crossing the diagram?
- Where can one find the following compositions (all values as % mol):
  A: $15\% H_2O$, $10\% Toluene$, $75\% Acetone$
  A: $40\% H_2O$, $50\% Toluene$, $10\% Acetone$

1-stage extractor

As production engineer, you are responsible for a pharmaceutical plant, were toluene is used as a solvent. Acetone is added to receive a final mixture of 5% mol acetone. Unfortunately, one of your employees poured too much acetone into tolune because he was distracted by a young accountant passing by, so that you find a mixture of 30% mol acetone and 70% mol toluene (50 kg in total). The unwanted acetone has to be removed. You decide to use water as an extraction agent. Your employee can add the water, mix it well and decant the two phases afterwards. How much water does he have to add?

cross current extractor

After yesterdays accident you are fascinated by extraction and order your employee to prepare the same mixture as yesterday. However, this time you will use a 3-stage cross flow extractor. For every stage you will add approximately one third of the water that you added in the previous one stage process. You are really curious to find out if you can reach an even lower acetone concentration?

- Draw a short scheme of the cross flow process
- Solve the problem graphically (use diagram)

counter current extractor

As your CEO finds your results very interesting too, he orders you to design an extractor for a continuous flow of $100\frac{kg}{h}$ of the 30% mol acetone and 70% mol toluene mixture. The final acetone concentration must not exceed 5% mol. The feed to water ratio shall be 1:4 in moles.

- How many stages will be needed?
- After a graphical solution, check your streams and compositions by using a mass balance!

General questions on extraction

- What is the main problem of extraction?
- In which cases is it a good idea to use extraction?
- Draw two 3-component-diagrams: One for a system were extraction is not possible, one diagram where extraction should work!
- Discuss the effect of the slope of tie lines on extraction!

Hydrodynamics

A high specific surface allows to increase the mass transfer, thus improving the extraction efficiency. The common method is to generate small droplets of one phase that are dispersed in the other, continuous phase, as in the stirred column used in this laboratory. Interactions between droplets and droplets and with the continuous phase result in complex fluid dynamic problems that are usually treated using empiric equations. Main factors to be considered for the operation of a extraction column are:

- **Droplet size**: Droplets usually range into the mm region. Big droplets can not provide a sufficient sized specific surface, whereas smaller ones result in high demand of energy for the dispersion process. Furthermore, the velocity of the droplets decreases with decreasing size; the operating limit of the column is reached when the droplets are too small to move and it is defined as the flooding point.
- **Droplet size distribution**: A uniform droplet size distribution is desired in order to increase efficiency. Furthermore due to the fact that most calculations are done with a mean droplet diameter the results are more accurate for a uniform droplet size distribution. However, the droplet size may change along the length of the column.

- **Holdup**: The total volume of all droplets (or the volume of the disperse phase) divided by the total column volume is called holdup ϵ. If operation conditions are set close to the flooding point of the column, the holdup increases and may not be stabilized any more.

$$\epsilon = \frac{V_{disperse}}{V_{disperse} + V_{continuous}}$$

- **Axial dispersion**: Axial dispersion follows from different phenomena, e.g. turbulence or differences in the droplet sizes, and results in lower column efficiency.

All these factors prevent a direct modeling approach of an extraction process, which is therefore usually designed with the help of empiric models. Two common design techniques will be discussed briefly.

Design concepts for multi stage extractors

As for the most thermal separation processes, two design techniques can be distinguished:

- based on mass transfer.
- based on equilibrium stages.

The design based on mass transfer is mathematically more complex and requires more information about hydrodynamics and property data. The calculation in a simplified case is discussed below. For the design based on equilibrium stages several methods exist, which differ in their assumptions and therefore in the accuracy and modeling complexity. The main methods are:

- McCabe-Thiele diagram (graphical).
- Kremser equation (analytical).
- graphical method in the ternary diagram.
- rigorous process simulation (e.g. Aspen).

Below only the method applying the McCabe-Thiele diagram is discussed. During the laboratory a short introduction to the method using the ternary diagram will be given and can be found in [1]. For the McCabe-Thiele method as well as for the simplified mass transfer calculation it is assumed that the phase flows are constant over the whole column. Therefore mass loadings ($Y : [\frac{\mathrm{kg_B}}{\mathrm{kg_A}}]$, $X : [\frac{\mathrm{kg_B}}{\mathrm{kg_C}}]$) and mass flows of A (called $\dot{F}$) and C (called $\dot{S}$) are used in the following. Assuming very low solubility of A and C, the flows $\dot{F}$ and $\dot{S}$ can be assumed constant.

HTU-NTU concept - a mass transfer concept

If the volume of a column can be regarded as a continuum, average mass transfer exchange rates are used for design purposes. In the easiest case, one assumes that two non-miscible flows are passing each other as plug flows along the column. Phase velocities are regarded as constant over the whole length of the column. Using a differential balancing approach and integration over the whole length of the column yields in:

$$H = \frac{\dot{S}}{K_X a A} \int_{X_{out}}^{X_{in}} \frac{1}{X - X^*} dX = \frac{\dot{F}}{K_Y a A} \int_{Y_{in}}^{Y_{out}} \frac{1}{Y^* - Y} dY$$

where H is the height of the column, A the cross section of a column, a the specific surface, K_X and K_Y the mass exchange coefficients, and X^* and Y^* are phase equilibrium loadings (X^* is the loading of the solvent phase in equilibrium with the actual loading of the feed phase and vice versa).
Referring to the solvent phase, the term $\frac{\dot{S}}{K_X a A}$ is called HTU which stands for height of a transfer unit. The integral is called NTU which stays for number of transfer units. The same is true referring to the other phase, which results in different numbers for the NTU and HTU values.
The NTU integral is usually solved numerically. It describes the thermodynamic separation behavior and is a measure how difficult the separation is. Typically, Y^* is expressed as a function of X. The HTU value depends on the flows and the column parameters (specific mass transfer area etc.) and describes how effective the column works. Knowing both values the required height of a column can be calculated $H = \mathrm{HTU} \cdot \mathrm{NTU}$.

Equilibrium stage concept

Comparable to distillation or absorption, the McCabe-Thiele diagram can be used in extraction to determine graphically the theoretical number of equilibrium stages. This requires the knowledge of the equilibrium line and the operating line. The equilibrium loading Y^* is generally given as a function of X:

$$Y^* = \mathrm{f}(X)$$

By means of a mass balance of component B the operating line can be calculated:

$$Y = Y_{in} + \frac{\dot{S}}{\dot{F}}(X - X_{out})$$

Figure 3 illustrates a typical construction in a McCabe-Thiele diagram. It is worth repeating that loadings ($Y : [\frac{\mathrm{kg_B}}{\mathrm{kg_A}}]$, $X : [\frac{\mathrm{kg_B}}{\mathrm{kg_C}}]$) instead of mole fractions are used and that for the operating line the pure mass flows of A (called $\dot{F}$) and C (called $\dot{S}$) are taken.
Once the number of theoretical equilibrium stages N_{eq} is known, the HETS value (HETS: height equivalent of a theoretical stage) or the efficiency of a real stage η can be used to calculate the column height H or the number of real stages required N, respectively:

$$H = \mathrm{HETS} \cdot N_{\mathrm{eq}}$$

$$N = \frac{N_{eq}}{\eta}$$

Please note that in our case, we are **NOT** using an **equilibrium stage** column as we do not have separated stages. In our case, the column is comparable to a constant counter-current stream with zones of higher and lower mixing intensity.

Experimental part

In the scope of this lab course, the toluene-acetone-water system will be considered, i.e. acetone (B) will be extracted from toluene (A) with the solvent water (C). The equilibrium of this system

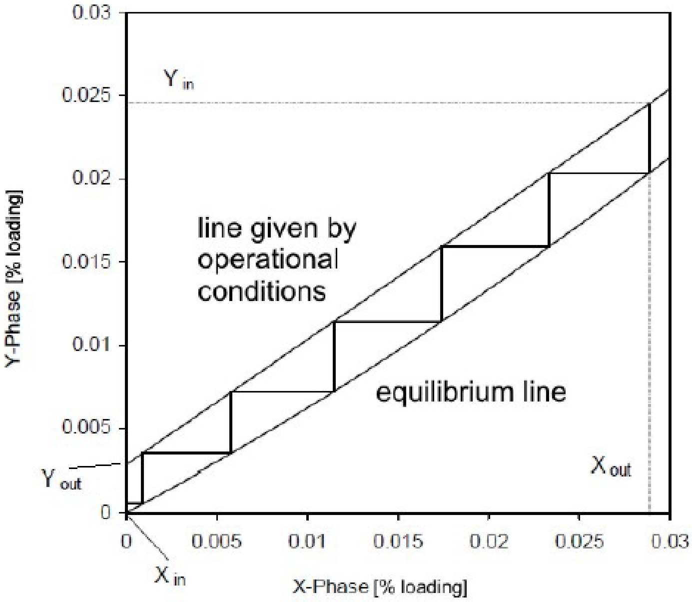


Figure 3: McCabe-Thiele diagram with equilibrium and operating line.

is given by the following equation:

$$Y^* = 0.573X + 5.066X^2 - 17.17X^3$$

The experimental setup and procedure will be described in the following sections.

Laboratory equipment

Figure 4 shows a scheme of the laboratory setup.
A stirred column (1) is used for the extraction (column type Oldshue-Rushton). Two tanks (3) hold the feed (toluene and acetone) that is pumped (5) to the column, fresh water from the tap is used as the solvent. Several valves and pumps (5) allow for setting up different experiments. Flow rates are indicated by rotameters (4). The filling level of the column is being controlled by a siphon (7). Once the toluene has left the column it flows through a (safety) water separator (6) and back to the tanks (3). As toluene has a lower density, the toluene flow direction is from bottom to top. For safety reasons, the continuous phase is always water and the organic phase toluene is dispersed. More details about the operation will be given during the laboratory. During start-up and shut-down of the equipment as well as when you reach the flooding point (stirring speed > 250 rpm) an assistant should be always at the column!

Measurements

During the laboratory, two issues will be investigated. The first part deals only with hydrodynamics whereas in the second one the extraction performance is studied. For both parts the flow rates are kept constant at $30\frac{l}{h}$ and $20\frac{l}{h}$ for toluene and water respectively.

1. The **holdup** will be measured at different stirring speeds. For this the glass valve in the lower half of the column is opened and a 100 ml cylinder is filled with dispersion.

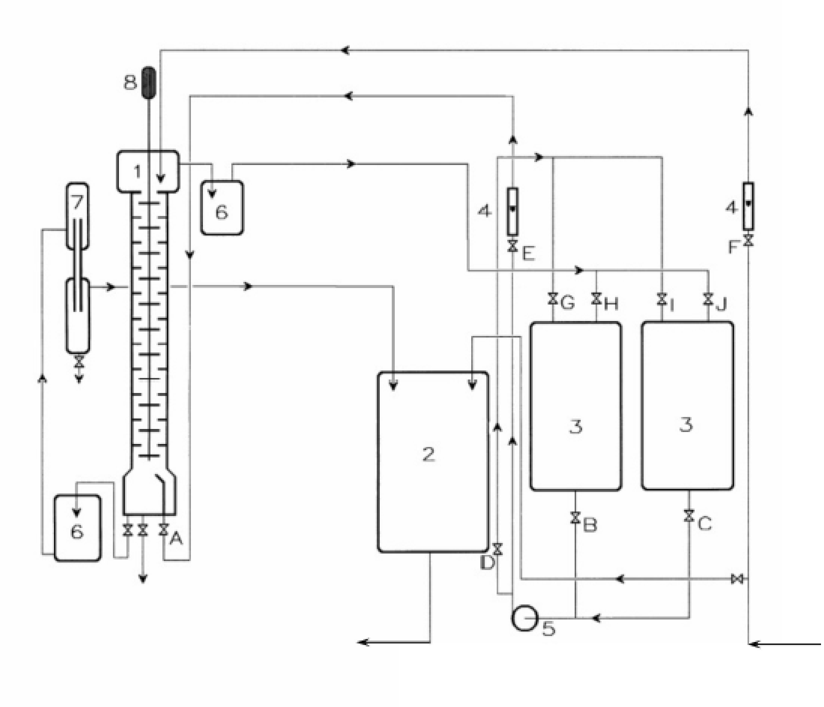


Figure 4: 1: column, 2: tank (aqueous), 3: tank (organic), 4: rotameter, 5: pump, 6: decanter, 7: filling level control, 8: stirrer motor.

After waiting for settling of the two phases, the volume of toluene and the total volume is measured. This measurement is repeated at stirring speeds of 50, 100, 150, 200, and 250 rpm. After changing the stirring speed the conditions in the column have to reach a steady state, therefore it is important to wait for about 15 minutes before taking the next sample. At stirring speeds slightly larger than 250 rpm the column is expected to reach flooding conditions. Therefore, after taking the sample at 250 rpm the stirring speed is increased very slowly until the flooding point is reached (an assistant should be at the column). For this part only water and toluene (without acetone) are used.

2. The **extraction performance** is studied at different stirring speeds. Acetone is added to the toluene to obtain a concentration of approx. 2-3 wt%. The stirring speed is increased stepwise (50, 100, 150, 200, and 250 rpm) and samples from the two outlet streams are taken. Additionally, one sample is taken from the feed in order to obtain its exact composition. The samples can be taken from the pipes using a syringe at the provided places. The samples are collected in vials and will be analyzed by GC during the following week. Please note that due to the high volatility of acetone, samples have to be sealed.

Report

After the successful completion of the laboratory work, a short report has to be prepared. The report should consist of the following sections:

- Introduction and brief explanation of extraction as a separation process (about 1 DIN A4 page).

- Experimental procedures and setup (about 1 DIN A4 page).
- Results and discussion (detailed analysis of the experiments). This section should give a comprehensive answer to the following questions:
    1. Plot the hold-up versus the stirring speed.
    2. Do you expect an increase or a decrease of the hold-up with increasing stirring speed? Based on the theoretical part during the laboratory course, explain why you expect a decrease or an increase.
    3. Is the plot in line with your expectations? If not, specify the measurements that don't match with the expectations. What could be the causes for the deviations?
    4. Do you always expect a better purification of your feed stream by increasing the stirring speed?
    5. Plot the extract and raffinate composition versus the stirring speed. Does the plot confirm your expectations?
    6. For the 5 operating points, determine the number of theoretical stages (NTS) with the McCabe-Thiele method.
    7. Calculate the slopes of the operating lines for the 5 operating points. Which value do you expect? What could be reasons for possible deviations?
    8. Plot the number of theoretical stages versus the stirring speed.
- Perform a theoretical analysis of an extraction process by solving the exercise presented earlier on page 3 and 4.

Data

Densities

- Density of water: $998 \frac{kg}{m^3}$
- Density of toluene: $866 \frac{kg}{m^3}$
- Density of acetone: $790 \frac{kg}{m^3}$

The extraction column

- Length of the stirred section: 1 m
- Column diameter: 73 mm; Stage height: 50 mm
- Free cross section area of the stators: 38 %
- Number of stirrers: 19
- Stirrer diameter: 50 mm; Stirrer height: 10 mm

Rotameters

The two rotameters have been calibrated for water and toluene. Figure 5 can be used to determine the set-value of the rotameters at the desired volume flows.

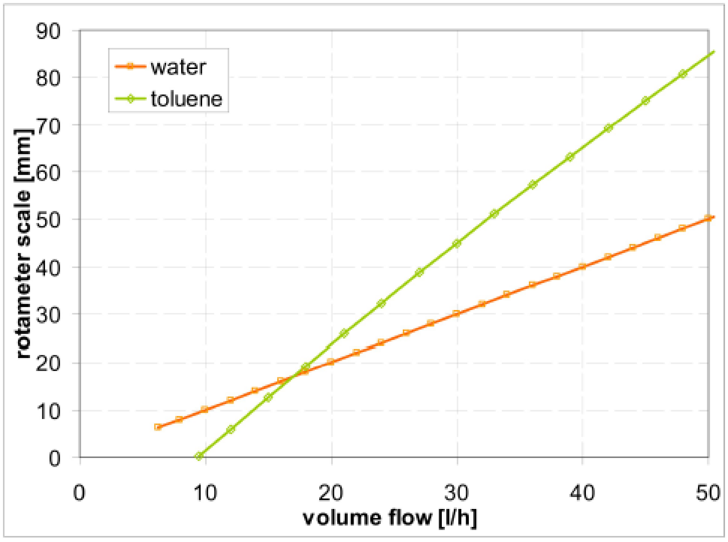


Figure 5: Rotameter calibration data.

References

[1] Mazzotti, M.: *"Hyper-TVT: http://www.hyper-tvt.ethz.ch/extraction-page.php"*, ETH, Zuerich, 2009.

[2] Wankat, P. C.: *"Separation Process Engineering"*, Chapman and Hall, London, 2006.

Assistance:

Ian Varela de Albuquerque
ML G24
varela@ipe.mavt.ethz.ch

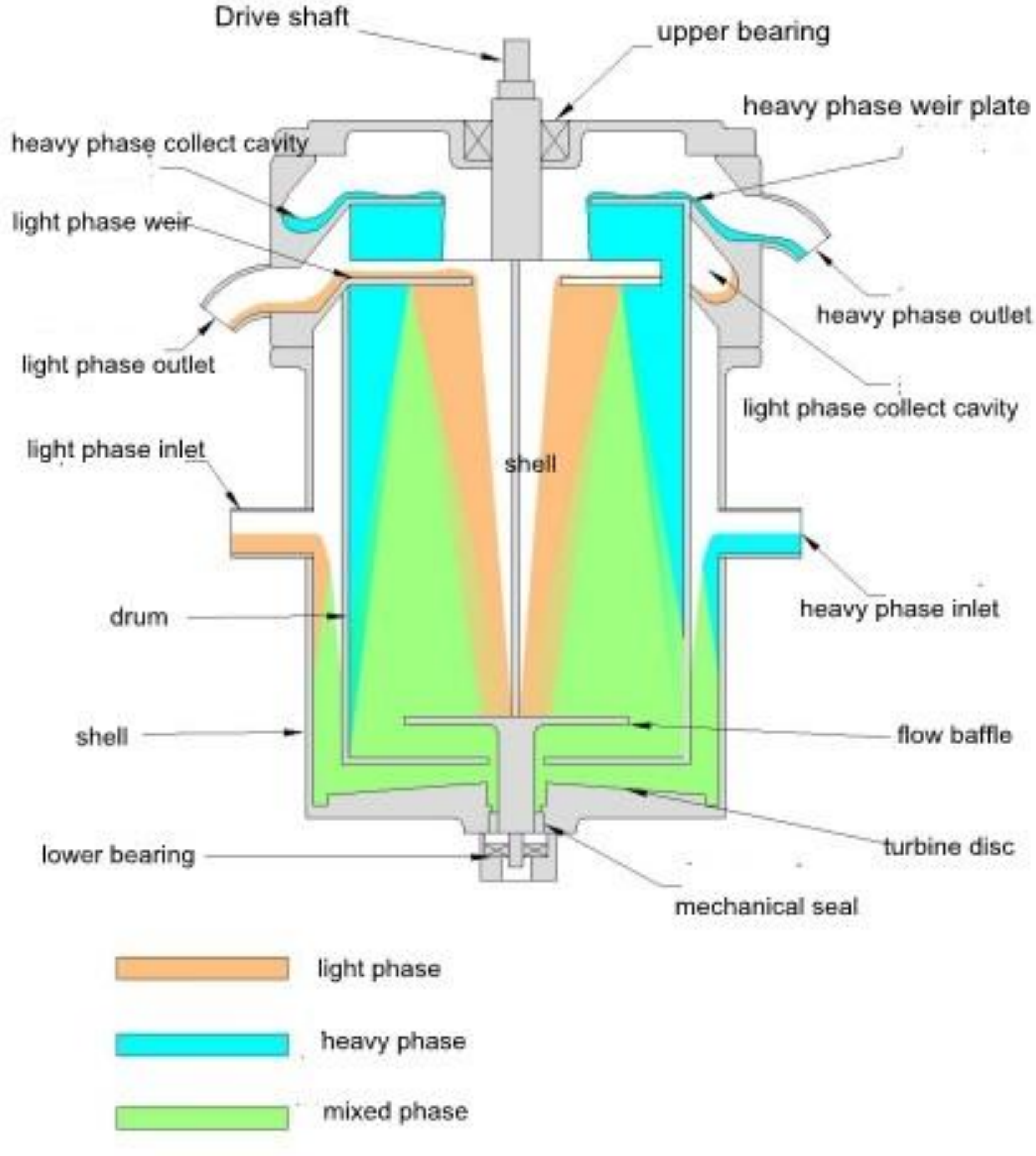
Daniel Sutter
ML G16
sutter@ipe.mavt.ethz.ch

2.12 Metal recycling by Single-Stage LLE

2.12.1 Single stage extraction liquid liquid extraction:

Product category: multistage counter-current extraction device, multistage cross current extraction device, single stage centrifugal extractor.

single stage extraction liquid liquid extraction is a new type, fast and highly efficient liquid-liquid extraction separation equipment, it is different with traditional extraction equipment such as mixer settler, extraction tower. Centrifugal extractor using the motor driven drum to reach high speed, the densities of different and not mutually mixed solution of two liquids in drum or blade rotation shear stress under complete mixing and mass transfer, and in high-speed rotation drum of centrifugal force under the action of rapid separation



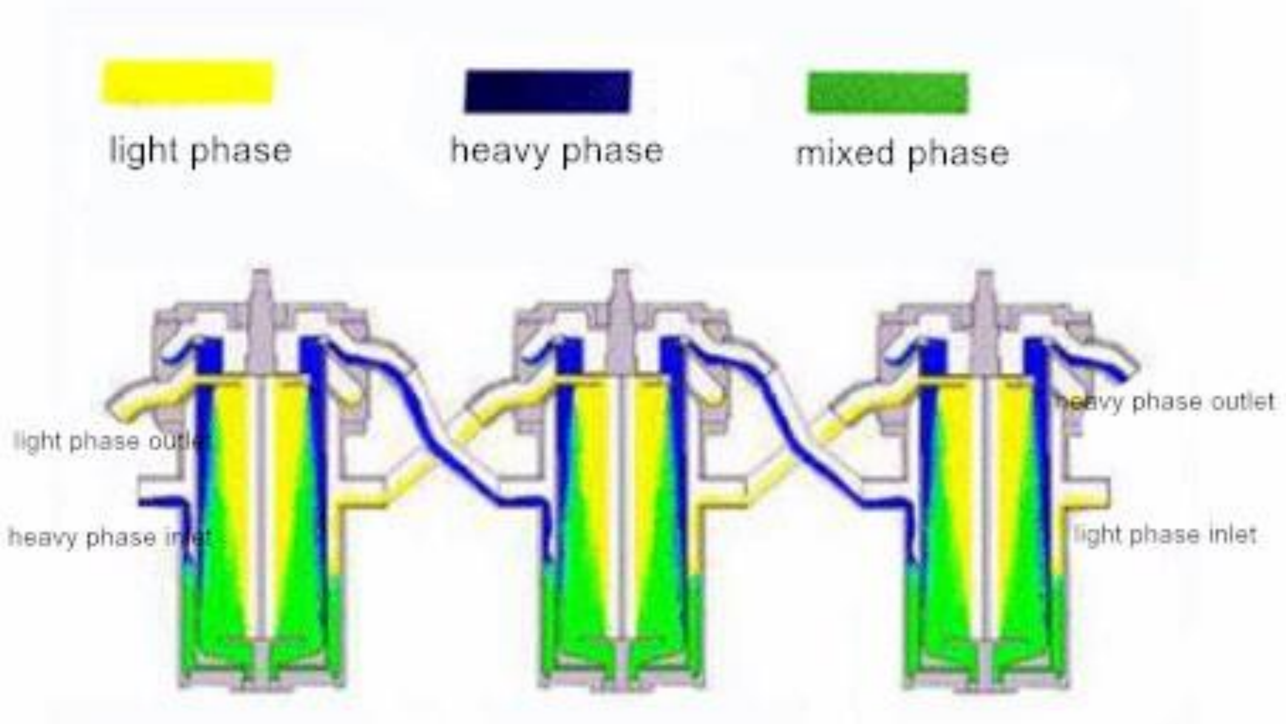
2.12.2 Centrifugal extraction work principle:

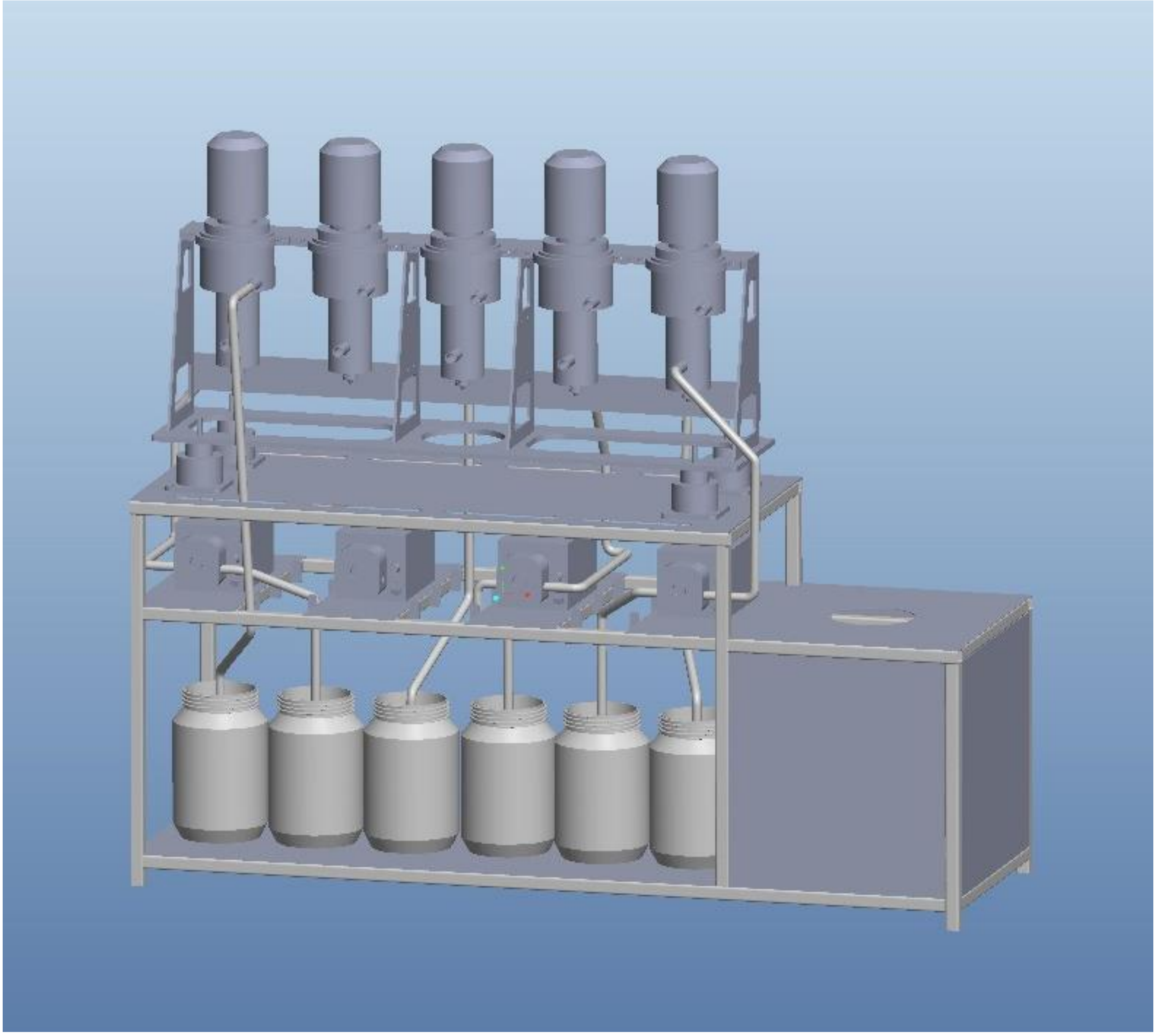
1. Mixed and mass transfer process

The two solution according to a certain proportion mix together, the two-phase dispersing, two-phase solution obtained sufficient mass transfer, mixing and mass transfer process is completed.

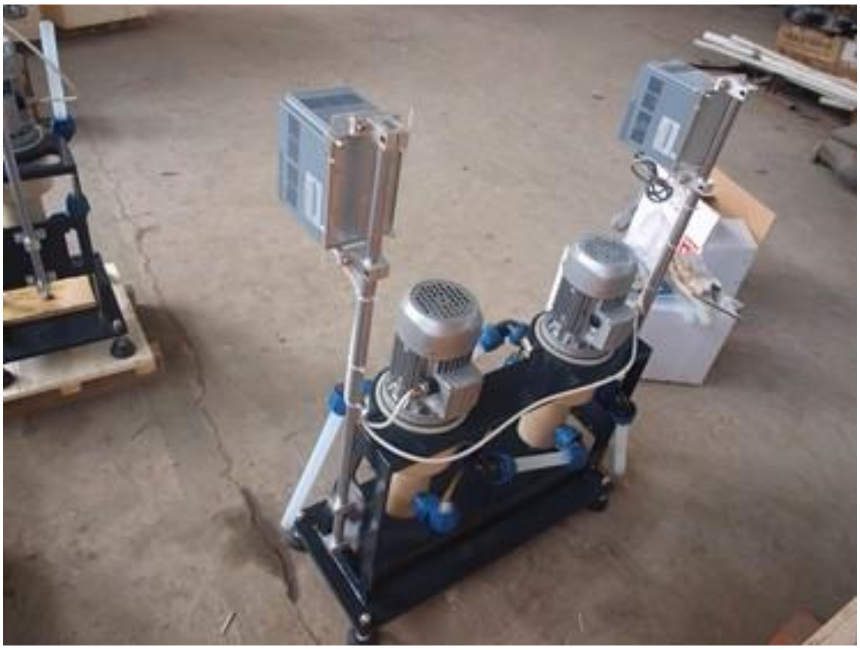
2. Two phases separation process

Mixed fluid in vortex disc or feeder into the drum,stay in certain area, mixture quickly and synchronizing drum rotary, under the action of centrifugal force, serious than liquid to flow in the process of gradually away from the drum center and leaned close to the drum wall; a small proportion of the light phase liquid gradually away from the drum wall and leaned toward the center, clarification of the two-phase liquid were eventually through their respective weir plate into collecting chamber and the draft tube are respectively extracted from the machine and complete phase separation process.





Detailed Images



Product Model

Model	Drum dia (mm)	Flux peak (L/H)	Inlet dia (mm)	Power(kw)	Size(L*W*H)mm	Weight (kg)
CWL50-M	50	50	DN20	0.18	400*400*800	18
CWL150-M	150	1000	DN40	0.75	620*630*1150	120
CWL250-M	250	3000	DN50	1.1	750*750*1400	460
CWL350-M	350	8000	DN65	1.5	950*950*1688	680
CWL450-M	450	15000	DN80	2.2	1000*1000*1800	880
CWL550-M	550	30000	DN100	3.0	1200*1200*1760	1100
CWL650-M	650	60000	DN125	4.0	1350*1350*1960	1800
CWL800-M	800	100000	DN150	5.5	1600*1600*2400	2500

1. Equipment material will be chosen according dto the feed physico-chemical property, common used SS304/316L/904L, common composite material, fluoride material and so on;
2. Above table is general parameter, real device has a little devitation, please refter to the matched technological manual;
3. Above flux is under ideal condition, ratio of oil and water is their flux sum when 1:1.

Product application

2.12.3 Application of single stage extraction liquid liquid extraction :

1. Oil water separation(crude oil/heavy oil/diesel and so on except water, salt);
2. Pharmaceuticals(such as used for ethyl acetate, methylene dichloride, normal butanol, choroforom and so on);
3. Extraction of chinese traditional medicine;
4. Pesticide(malathion extraction and so on);
5. Bioengineering(nutrient solution extraction and interferon extraction and so on);
6. Chemical and fine chemical(catalyst extraction and so on);

7. Hydrometallurgy(used mutilstage extraction and back extraction and so on to extract nickel, copper, uranium and other rare metals);
8. Food(edible oil, spice, refined oil, food color and so on);
9. Perfume industry;
10.Printing and dyeing industry(printing and dyeing wastewater treatment and recycle);
11.Environmental protection(used multistage extraction and back extraction and so on technology to treat wastewater with phenol, oil-water separation of marine sewage, groundwater separation or extraction or purification and so on);
12. Cosmetics industry(to extract nutrient ingredient);
13. Liquid/two gas phase separation(to remove bubble in liquid phase and so on).

Our Company

2.12.4 Zhengzhou Tianyi Extraction Technology Co.,Ltd.

Zhengzhou Tianyi Extraction Technology Co.,Ltd(short for ‘TIANYI EXTRACTION’) was established in 2005, and mainly specialized in developing, manufacturing liquid-liquid separation and mixing equipment centrifugal extractor and extraction groove. TIANYI EXTRACTION have more than 100 staff, and already obtained more than 20 patents, and have more than 30 sets processing machinery. Now we have one application research center, one pilot-plant experimental base for extraction (expanding test), two modern production and processing center, and already got the certificate of ISO9001 and CE certification. In 2016, we obtain the prize of “High-Tech Enterprise”, our product are mainly used in industries such as fine chemical, Hydrometallurgy, Pharmacy and Environmental protection and so on. Tianyi has strong R&D& Manufacturing strength, and excellent quality positioning, and perfect service after-sales system, leading domestic and foreign indsutries. Taken the management idea of integrity, professional, practical, innovation. And according to advanced processing equipment, strict quality control system, high-quality technical team and perfect after-sell services. TIANYI EXTRACTION dedicate to provide a full technical solution. Taken “Mutual benefit and Win-Win” as our aim, TIANYI EXTRACTION will provide you a high quality service.

Certifications

This series extractor is our the 4th product with our independent intellectual property rights, and patent number: ZL2014205865573. Under the same handling capacity, this series of machine energy consumption is 10%～30% of traditional annular type. At the same time, and it has short duration, split phase velocity, high extraction rate, save cost and solvent could be recycled and reused.

Our Service & FAQ

2.12.5 Our service

1. R&D, manufacture and sale on extraction and mixing equipment;
2. contraction on related supporting project, such as planning layout on extraction production line, installation and adjustion on extraction equipment, construction on related construction facilities.
3. Project test in every stage, such as lab-scale test, pilot test etc.

2.12.6 FAQ

Q1. Are CWL-M serious centrifugal extractor fit for our liquid?

A: CWL-M series extractor are widely used in liquid liquid extraction or separation. Liquid liquid extraction, using the the difference of solubility and distribution coefficient of two materials, transfer the solute from one solvent to another solvent. CWL-M series centrifugal extractor mainly used in industries such as oil water separation, pharmacy, pesticide, hydrometallurgy, environmental protection etc. So if your process is liquid liquid extraction and no solid, you can use our centrifugal extractor.

Q2: How do we judge the treatment effect of CWL-M centrifugal extractor?

A: we have research center in our company, to provide client test before sale and extraction process etc, in our research center, we have more than 20 centrifugal extractor for laboratory or pilot test, and after some years test, we have accumulated many experience on hydrometallurgy, chemical, pharmacy industries. We welcome you to visit our research center for laboratory or pilot test.

Q3:What is the difference between CWL-M series centrifugal extractor and others?

Right now, most centrifugal extractor in the market are traditional annular centrifugal extractor, CWL-M centrifugal extractor are our forth generation product(patent ZL2014205865573) and have advantage such as no bottom bearing and seal, no leakage risk, free maintenance; more energy saving, only 1/3~1/10 power consumption of traditional equipment; our equipments’ material are perfluorinated polymer materials, corrosion resistance to strong sulfuric acid, hydrochloric acid, mixed acid.Applied to easily emulsifying system, mix thoroughly and high efficiency.

Q4: How do we choose suitable centrifugal extractor?

A: There are five issues that must be take seriously when election:

(1).Dimension and power
(2).Anti-corrosion property
(3).Anti-explosion property
(4).Equipment structure
(5).Environmental protection
(6) Price.

The main distinguish is property and configuration. Some extractor with heater or more control program. Sometimes spare parts cost is higher than main engine. When choose, except main engine, you should pay more attention on the rotor(quantity and species), the necessary material, bowl, wire structure and so on. All of these included are the complete price of full centrifugal extractor.

Q5: Are CWL-M series centrifugal extractor anti-explosion and automatic controlled?

We can equip related anti-explosion and automatic control function as per client necessary.

......

If you were not satisfied, please feel free to return, and the back goods freigth we shall bear!

Contact Manager: Annie

Tel:+86 15237168511

Wechat: muzi5279

Email: annie10@cncuiqu.com

2.13 Commercial LLE extraction column (Made in China)

Overview

Quick Details

Condition: New

Type: Extraction Equipment

Product Type: liquid liquid extraction column

Place of Origin: Henan, China (Mainland)

Brand Name: TIANYI

Model Number: RDC-1000

Voltage: Customized

Power(W): standard

Weight: standard

Dimension(L*W*H): dia80*1000mm

Certification: ISO9001/CE

Warranty: 12 Months

After-sales Service Provided: Engineers available to service machinery overseas

Function: immiscible liquid liquid extraction

Capacity: 1-60000L/h

Application: Chemical&pharmacy&hudrometallurgy&envrionmental protection etc

Operation: Continuous

Material: SS/Fluorine/Compoiste

Machine name: liquid liquid extraction column

Company type: R&D&Manufacturing

Corlor: Cutomized

Advantage: high stage efficiency

Continuous: continuous production

Packaging & Delivery

Packaging Details as per customer requirement
Delivery Time 30-60days

Product Description

Liquid-liquid extraction is a technically advanced, niche separation technology. It is applied when simpler alternatives such as distillation are not able to meet your requirements. Components are extracted from your feed with the help of a solvent, without an energy demanding evaporation step.

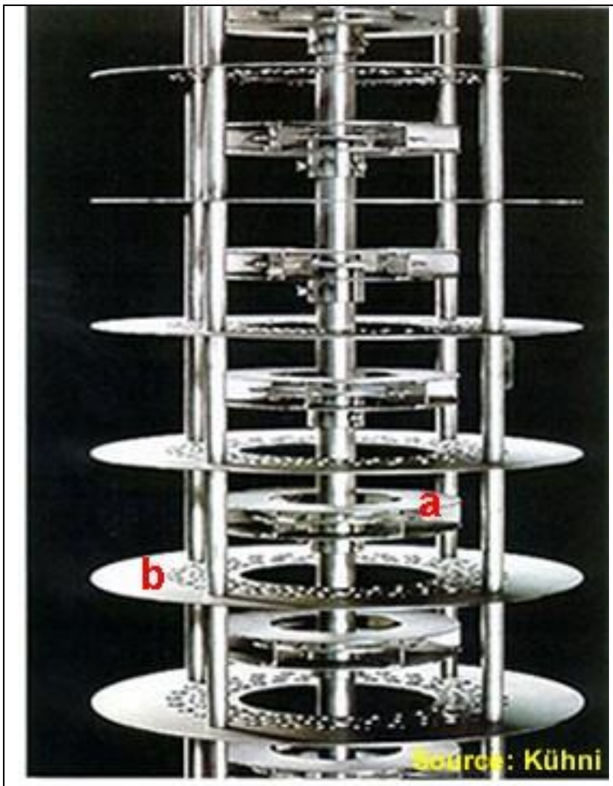
2.13.1 Liquid liquid extraction column introduction:

Extraction column is a kind of column extraction equipment of mechanical stirring, it is composed by upper settling chamber, emulsion chamber and bottom settling chamber. the emulsion chamber is cylinder type, and is divided into several extraction chambers by static ring baffle, there is a fixed turnplate between two static ring baffles, and rotating with shaft together. When work, heavy phase(aqueous)and light phase(organic phase) enter the equipment from column top and bottom respectively, and contact countercurrently in column. Under fixed turnplate stirring, the dispersed phase formed small droplets, to enlarge mass transfer area and finished extraction process,and then Heavy phase and light phase discharge from the different exit.

2.13.2 Liquid liquid extraction column characteristics:

1. Cover a small area, low maintenaince cost;
2. Large capacity, suitable for continuous production;
3. High stage efficiency, small solvent sluggish flow

Detailed Images


a
b
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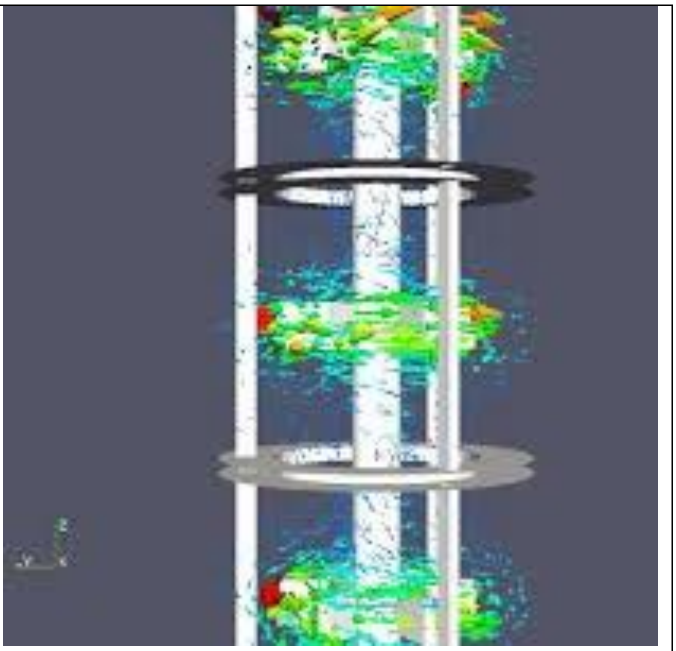

Product Model

Model	Column Model(mm)	Valid Height(mm)
RDC-50	Dia 80	1000
RDC-80	Dia 80	1000
RDC-100	Dia 100	1000/1500
RDC-150	Dia 150	1500/2000
RDC-200	Dia 200	Customized
RDC-300	Dia 300	Customized
RDC-500	Dia 500	Customized
RDC-1000	Dia 1000	Customized

1. The common material is transparent organic glass, PP, Hard PVC, glass, stainless steel etc;

2. Above technology parameters are experiment parameter, the special application will be designed accoprding to customer's requirement.

Product application

2.13.3 Liquid liquid extraction column application area:

1. Separation of systems with similar boiling points（e.g., separation of aromatics from aliphatic hydrocarbons)

2. Separation of high boiler and low-con-centration solutes from aqueous solutions(e.g., phenol)

3. Separation of mixtures with high boiling points (e.g., vitamins)

4. Separation of temperature-sensitive compounds (e.g., acrylates, biotechnology)

5. Separation of azeotropic mixtures(extraction of acetic or formic acid from aqueous media using,e.g., MTBE as solvent)

6. Extraction of organic compounds from salt solutions (e.g., caprolactam)

7. Extraction of salts from polymer solutions (e.g., ketone resins, polyols)

8. Extraction of metal salts from low-grade ores(e.g., copper)

Liquid-liquid extraction is expected that importance of solvent extraction will increasae as the feedback of chemical processes changes from crude oil to biomass. The components obtained in the first processing steps from biomass have more functional groups and are less volatile than the key components obtained from crude oil.Thus, it maybe economically more attractive to use extraction with suitable solvents (including extractants like ionic liquids) than to use distillation at low pressure.

Our Company

2.13.4 Zhengzhou Tianyi Extraction Technology Co.,Ltd.

Zhengzhou Tianyi Extraction Technology Co.,Ltd(short for ‘TIANYI EXTRACTION’) was established in 2005, and mainly specialized in developing, manufacturing liquid-liquid separation and mixing equipment centrifugal extractor and extraction groove. TIANYI EXTRACTION have more than 100 staff, and already obtained more than 20 patents, and have more than 30 sets processing machinery. Now we have one application research center, one pilot-plant experimental base for extraction (expanding test), two modern production and processing center, and already got the certificate of ISO9001 and CE certification. In 2016, we obtain the prize of “High-Tech Enterprise”, our product are mainly used in industries such as fine chemical, Hydrometallurgy, Pharmacy and Environmental protection and so on. Tianyi has strong R&D& Manufacturing strength, and excellent quality positioning, and perfect service after-sales system, leading domestic and foreign indsutries. Taken the management idea of integrity, professional, practical, innovation. And according to advanced processing equipment, strict quality control system, high-quality technical team and perfect after-sell services. TIANYI EXTRACTION dedicate to provide a full technical solution. Taken “Mutual benefit and Win-Win” as our aim, TIANYI EXTRACTION will provide you a high quality service.

Our Service & FAQ

2.13.5 Our service

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2. contraction on related supporting project, such as planning layout on extraction production line, installation and adjustion on extraction equipment, construction on related construction facilities.
3. Project test in every stage, such as lab-scale test, pilot test etc.

2.13.6 FAQ: How to select solvent extraction agent of Liquid liquid extraction column?

The solvent is the key to a successful separation by liquid-liquid extraction. The several criteria are:

1. Distribution Coefficient This is the ratio (at equilibrium) of the concentration of solute in the extract and raffinate phases. It gives a measure of the affinity of the solute for the two phases. A

distribution coefficient other than unity implies that the solute must have different affinity in the two phases. If only one solute is involved (such as in the recovery of an impurity from an effluent stream), only the distribution coefficient need be considered, and it is desirable for this to be as large as possible.

2. Selectivity (Separation Factor) If there are more than one solutes (say two solutes A and B), then consideration should be given to the selectivity of the solvent for solute A as against B. The selectivity between the 2 solutes A and B is defined as the ratio of the distribution coefficient of A to the distribution coefficient of B. For all useful extraction operation the selectivity must exceed unity. If the selectivity is unity, no separation is possible.

3. Insolubility of Solvent The solvent should have low solubility in the feed solution, otherwise the separation is not "clean". For example, if there is significant solubility of solvent in the raffinate stream, an additional separation step is required to recover the solvent.

4. Recoverability It is always necessary to recover the solvent for re-use, and this must ordinarily be done by other means, eg. distillation. If distillation is to be used, the solvent should form no azeotrope with the extracted solute and mixtures should show high relative volatility. The solvent should also be thermally-stable under the distillation temperature.

5. Density A large difference in density between extract and raffinate phases permits high capacities in equipment. This is especially important for extraction devices utilizing gravity for phase separation.

6. Interfacial Tension The larger the interfacial tension, the more readily coalescence of emulsions will occur but the more difficult the dispersion of one liquid in the other will be. The more readily coalesces the emulsions the easier phase separation will be. Low interfacial tension aids dispersion and thus improves contacting mass-transfer efficiency. Coalescence is usually of greater importance, and interfacial tension should therefore be high.

7. Chemical Reactivity The solvent should be stable chemically and inert toward the other components of the system and toward the common materials of construction.

8. Viscosity, Vapour Pressure, Freezing Point These should be low for ease in handling and storage, for example, a high viscosity leads to difficulties with pumping, dispersion and mass transfer rate.

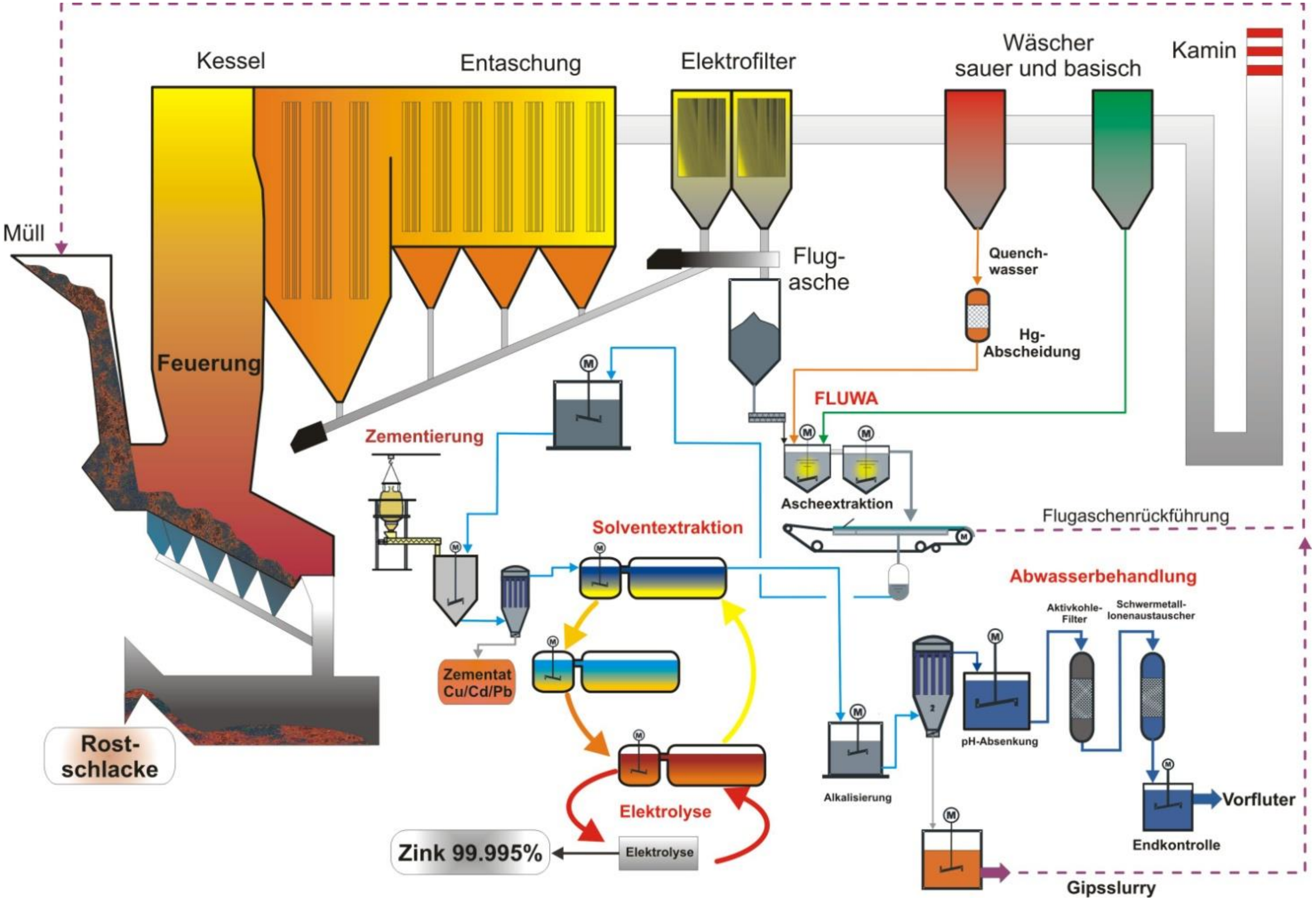
9. Availability and Cost An excellent solvent may not be commercially available. Or it may represent a large initial cost for charging the system, and a heavy continuing expense for replacing inevitable operating losses.

10. Other Criteria Toxicity and flammability of the solvent are important occupational health and safety considerations. Stability of the solvent (i.e. resistance to breakdown), particularly in the recovery steps, is significant, especially if the breakdown products might contaminate the products of the main separation. Corrosivity of the solvent leads to the usual problems with materials of construction. Finally, compatibility of the solvent with the mixture to be separated can have many manifestations, particularly when easily contaminated materials such as food or pharmaceuticals are being handled. Note: The solvent may not always be a single chemical species. For example, the most appropriate liquid may not have suitable physical properties for direct use as solvent. In

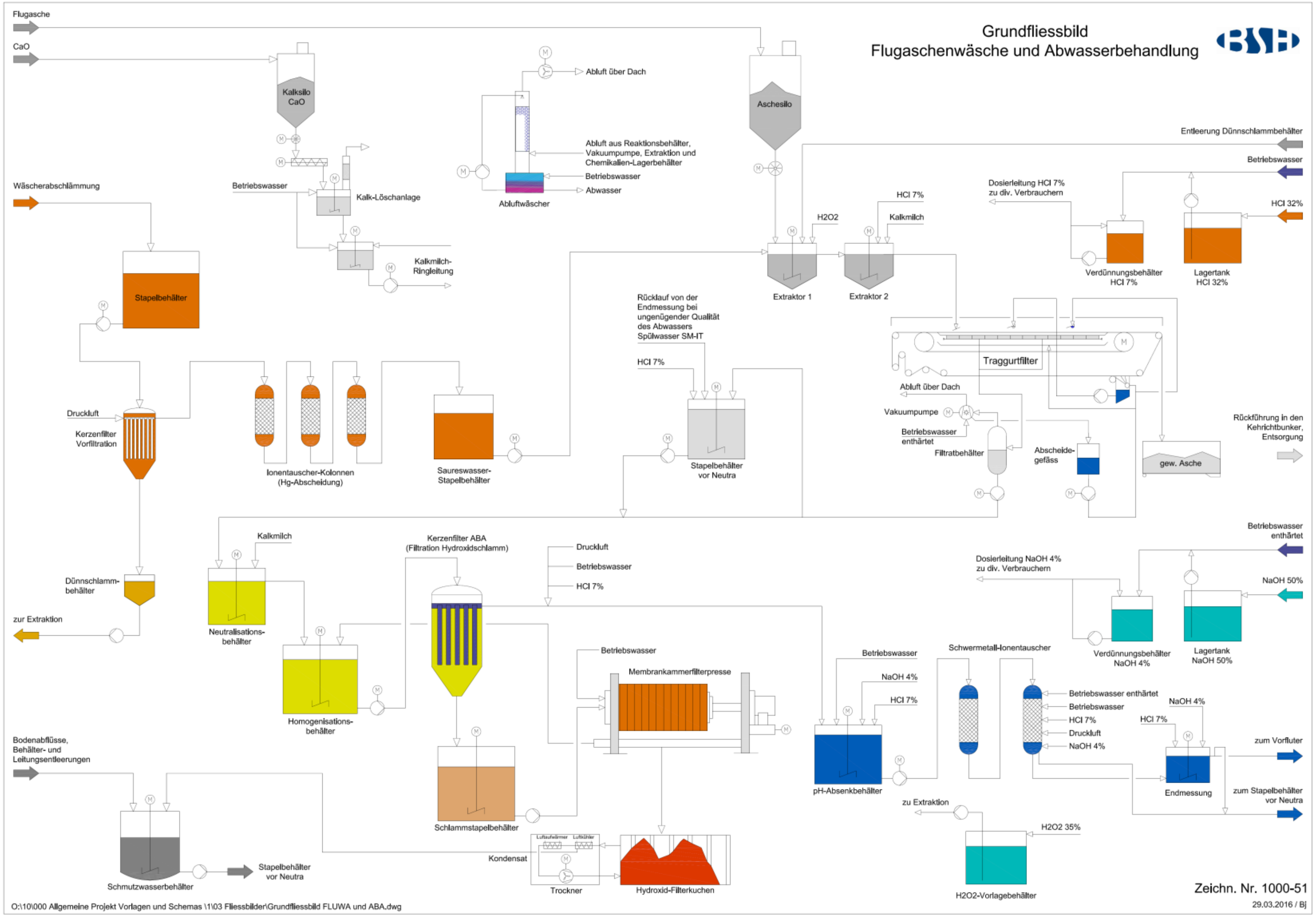
such cases it can be used dissolved in another suitable liquid. The active component of the mixture is then known as the extractant and the liquid in which it is dissolved as the diluent. The solvent comprises the two together.

2.14 Heavy Metals Recovery

2.14.1 pure Zinc recycling with FLUREC



2.14.1.1 FLUWA


Grundfliessbild
Flugaschenwäsche und Abwasserbehandlung
Flugasche
CaO
Kalksilo CaO
Aschesilo
Abluft über Dach
Abluft aus Reaktionsbehälter, Vakuumpumpe, Extraktion und Chemikalien-Lagerbehälter
Betriebswasser
Abwasser
Abluftwäscher
Wäscherabschlämmung
Betriebswasser
Kalk-Löschanlage
Kalkmilch-Ringleitung
Stapelbehälter
Entleerung Dünnschlammbehälter
Betriebswasser
Dosierleitung HCl 7% zu div. Verbrauchern
HCl 32%
HCl 7%
H2O2
Kalkmilch
Extraktor 1
Extraktor 2
Verdünnungsbehälter HCl 7%
Lagertank HCl 32%
Rücklauf von der Endmessung bei ungenügender Qualität des Abwassers Spülwasser SM-IT
HCl 7%
Traggurtfilter
Abluft über Dach
Vakuumpumpe
Betriebswasser enthärtet
Filtratbehälter
Abscheidegefäss
gew. Asche
Rückführung in den Kehrichtbunker, Entsorgung
Druckluft
Kerzenfilter Vorfiltration
Ionentauscher-Kolonnen (Hg-Abscheidung)
Saureswasser-Stapelbehälter
Stapelbehälter vor Neutra
Dünnschlamm-behälter
zur Extraktion
Kalkmilch
Neutralisations-behälter
Homogenisations-behälter
Kerzenfilter ABA (Filtration Hydroxidschlamm)
Druckluft
Betriebswasser
HCl 7%
Betriebswasser
Membrankammerfilterpresse
Schlammstapelbehälter
Betriebswasser enthärtet
Dosierleitung NaOH 4% zu div. Verbrauchern
NaOH 50%
Verdünnungsbehälter NaOH 4%
Lagertank NaOH 50%
Betriebswasser
NaOH 4%
HCl 7%
Schwermetall-Ionentauscher
Betriebswasser enthärtet
Betriebswasser
HCl 7%
Druckluft
NaOH 4%
NaOH 4%
HCl 7%
zum Vorfluter
zum Stapelbehälter vor Neutra
Endmessung
pH-Absenkbehälter
zu Extraktion
H2O2 35%
H2O2-Vorlagebehälter
Bodenabflüsse, Behälter- und Leitungsentleerungen
Schmutzwasserbehälter
Stapelbehälter vor Neutra
Kondensat
Lufterwärmer
Luftkühler
Trockner
Hydroxid-Filterkuchen
Zeichn. Nr. 1000-51
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O:\10\000 Allgemeine Projekt Vorlagen und Schemas \1\03 Fliessbilder\Grundfliessbild FLUWA und ABA.dwg

2.14.2 Zincex process (ion exchange process)[5]

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Hydrometallurgy Volume 70, Issues 1–3, July 2003, Pages 63-71:

Abstract

Solvent extraction separation of divalent metal ions, Cd(II) and Zn(II), with an organophosphorus extractant, D2EHPA (di(2-ethylhexyl)phosphoric acid), and an aqueous hexadentate ligand with nitrogen donors, TPEN (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine), was studied. The extraction process consists of two steps, namely, the complex formation between TPEN and the divalent metals in the aqueous phase, $M(TPEN)^{2+}$ (M=Cd or Zn), and the formation of a hydrophobic complex between $M(TPEN)^{2+}$ and D2EHPA in the organic phase. The stability constants for the formation of $Cd(TPEN)^{2+}$ and $Zn(TPEN)^{2+}$, which were measured by potentiometric titration technique, were evaluated as higher than 10^{13}. By the addition of TPEN in amounts equimolar with the divalent metal in the aqueous solution, more than 99% of divalent metal was coordinated with TPEN at pH above 2.5, where the protonation of TPEN is negligible. Under these conditions, the extraction of Cd(II) with D2EHPA was promoted; on the contrary, that of Zn(II) was depressed remarkably. TPEN acts as a synergist for the extraction of Cd(II) and a masking agent for that of Zn(II). Then, the separation factor of Cd(II) was increased by more than 500 times than that without TPEN. TPEN is an excellent synergist that functions by small additions in the aqueous solution and promotes extraction selectively for soft metals such as Cd(II).

2.14.3 The phase equilibrium of ternary mixtures

Solvent extraction, or liquid-liquid extraction is a separation technique

isothermal in a heterogeneous liquid medium.

The method is based on the existence of a difference in the solubility of a substance in two immiscible liquids. The process has three steps, as shown in Figure 1:

- Mixture of the two immiscible liquids, one of them containing the solute,
- Obtaining physico-chemical equilibrium, leading to demixing,
- Separation of the two new liquid phases obtained based on the difference of

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[5] K. Takeshita; K. Watanabe; Y. Nakano; M. Watanabe (2003). "Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN". Hydrometallurgy. 70: 63–71. doi:10.1016/s0304-386x(03)00046-x.

densities.

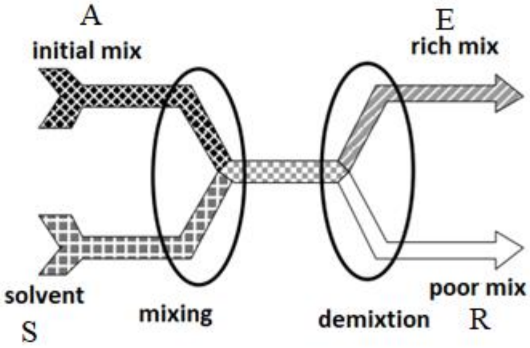


Figure 1 : *principle of a separation stage by obtaining a balance*

Practically, solute B dissolved in the diluent A is contacted with the solvent S. The solute B, generally more soluble in the solvent than in the diluent, passes from the solution in the solvent, the solvent enriched in solute is the extract E while the diluent depleted solute is the residue (or raffinate) R. The passage of solute B from diluent A in solvent S takes place as long as the equilibrium physico-chemical is not reached. So that the driving force of transfer remains almost constant, the two liquids feeding the column flow against the current.

In order to transport the material as quickly as possible, the area of the transfer surface is increased by various artifices. These objectives can be obtained in a column.

2.14.3.1 The partition coefficient

A substance B placed in contact with two partially miscible solvents or immiscible S and A is distributed unequally between the two phases that are formed when the physicochemical balance is reached. The ratio of B concentrations in these two phases is the partition coefficient m.

2.14.3.2 The ternary diagram

At equilibrium, these biphasic systems are trivariant. At pressure and temperature constants, they can be represented in a system of triangular axes. The equilateral triangle has the advantage of allowing an equivalent representation for all the constituents. The right triangle has the advantage of being able to expand the scale of one of the axes. It is often interesting to limit the plot to the "useful" part. Each vertex of the triangle represents a pure component. The solute content B, in solvent S and diluent A is expressed in mol%, mass, volume, etc ... and is obtained by a suitable projection on the axis chosen as shown in Figure 2.

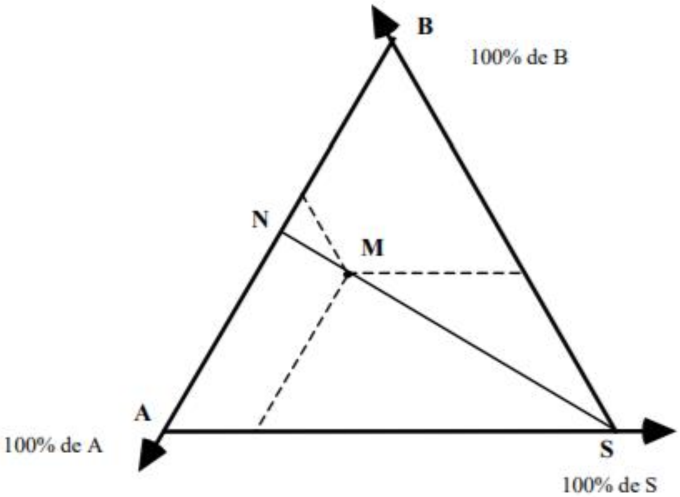


Figure 2 : ternary diagram

It is easy to demonstrate that the quantity of S and the quantity of the mixture N are in a ratio of the lengths of the MN and MS segments (rule of the lever arm) and that the quantities of two components are in the ratio of projections of the segments on the binary axis corresponding.

Conversely, if the mixture N is added a mass of solvent S, the ternary mixture

result is represented by the point M on the line NS such that:

$$\frac{mass\ of\ N}{mass\ of\ S} = \frac{MS}{MN}$$

2.14.3.3 The demixtion

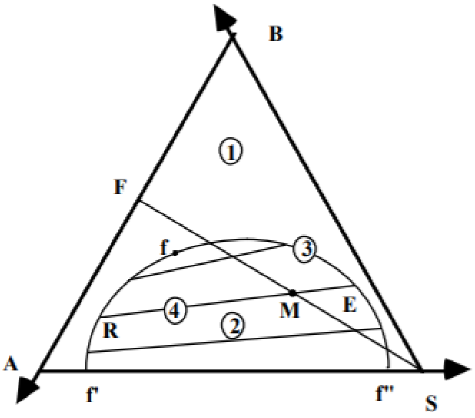


Figure 3 : Isothermal and isobaric demixing curve.

In a ternary system with limited mutual solubility zone (1) stable states, characterized by a complete miscibility, is separated from the zone (2) unstable states constituting the miscibility gap or diphasic zone, by the solubility isotherm (3) or line "Critical" or demixing curve or equilibrium curve or saturation curve.

Within the miscibility gap, no mixture can exist indefinitely:

any system whose overall composition is represented by point M is divided into two composition phases R and E, points at the intersection of the equilibrium line (4) or conodal RME and the demixing curve f'ff ". At the critical point f the two phases in balance have the same composition.

2.14.3.4 Solvent separation

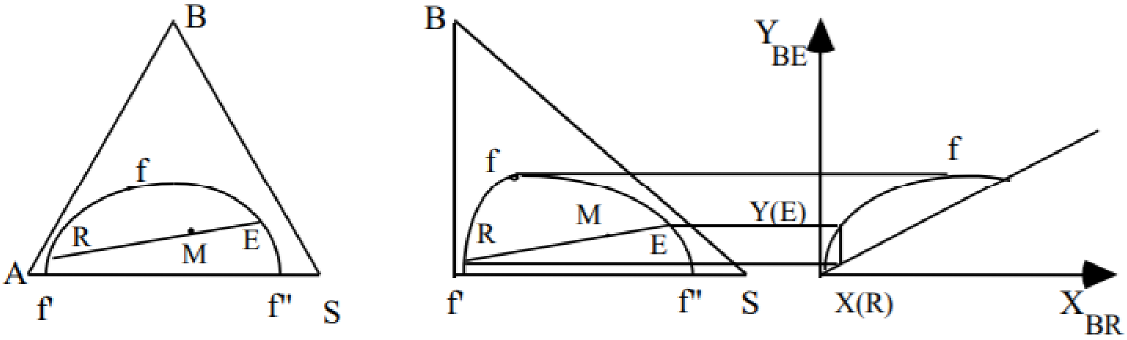


Figure 4 : Representation of a ternary system with limited miscibility

In the zone of total miscibility no separation can take place. However, if starting from an initial mixture F, by the addition of the solvent S, a system whose composition is global M lies within the miscibility gap, which separates into two phases R and E. Phase R, rich in diluent A is the raffinate, while phase E, rich in

solvent S, constitutes the extract.

In general, the concentration of solute B in the raffinate is designated by x and in

the extract by y. It is then possible to draw the distribution curve or equilibrium curve which represents y in terms of x.

2.14.4 Countercurrent extraction

2.14.4.1 The principle

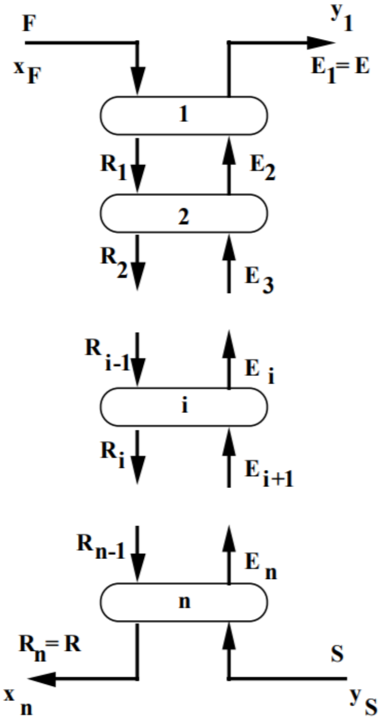


Figure 5 : diagram of countercurrent column

2.14.4.2 the material balance

The writing of the material balance makes it possible to know the composition of the global system and of each of the subsystems (stages).

Balance sheet on the column:

Global: $mF + mS = mE + mR = mM$

Solute B: mF xF + mS yS = mE y1 + mR xn = mM xM

This system of two equations with eight unknowns can be solved if six variables are otherwise known. In practice mF, mS, xF and yS (= 0) are imposed. By fixing two other variables, for example xn and mR, this system of equations can be solved.

Moreover, the combination of these relationships makes it possible to determine the position of the point M in the ternary diagram. Graphically, F and S determine M. The point M is both on the FS and ER lines. R (Rn)being known, E (E1) is obtained by the intersection of RM and the demixing curve. At point E1 the conodal matches R1.

Balance sheet on the stage i:

Global: $m_{R_{i-1}} + m_{E_{i+1}} = m_{E_i} + m_{R_i}$

Solute:

$$m_{R_{i-1}} x_{i-1} + m_{E_{i+1}} y_{i+1} = m_{E_i} y_i + m_{R_i} x_i$$

2.14.4.3 The existence of a pole P

The writing of the overall balance successively for the column and for each of the floors allows to show the existence of a pole P through which all RiEi + 1 lines pass.

Column: mR - mS = mF - mE = Cte = mP

The PRS and PFE points are aligned.

The FERS points being known, P is determined graphically.

Stage 1 : $m_{R_1} - m_{E_2} = m_F - m_E = m_P$

PR1E2 points are aligned. R1 being known, point E2 is in turn.

Step by step, it is possible to write:

Floor i: $m_{R_i} - m_{E_{i+1}} = m_F - m_E = m_P$

The points PRiEi+ 1 are aligned and the point Ri is known by the graphic construction previous point, the point Ei+ 1 is determined.

Gradually, all the points Ri and Ei are determined.

The construction stops when the right PRnS goes through R or "exceeds" R.

Each line RiEi constitutes a theoretical stage.

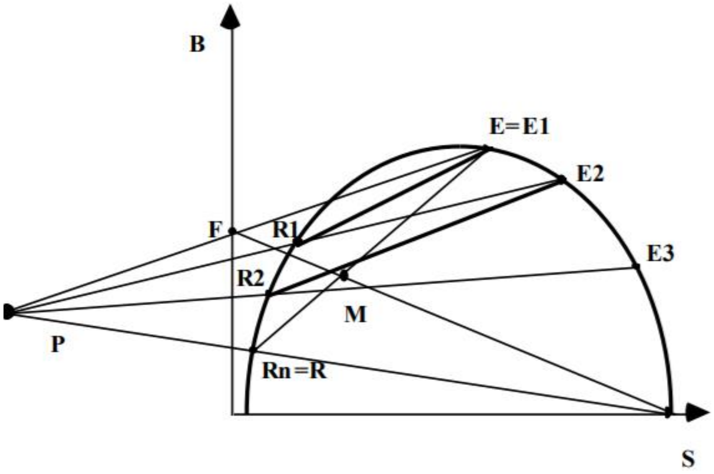


Figure 6 : Graphical construction of theoretical floors

2.14.4.4 Remarks

The previous graphical construction is easier if on the same graph the demixing curve and the operating curve.

If an operating line passing through P was confused with an equilibrium line EiRi it then an infinite number of theoretical stages would be required. The ratio of the mass of solvent to that the power supply would then be the minimum usable to effect the separation. In practice we consider the equilibrium line passing through F as confused with the straight line passing through P. The intersection of the lines FS and E1minRn gives the point Mmin hence the value of the ratio (mS / mF) min.

The choice of the value of the solvent rate p = mS / mF is done by taking:

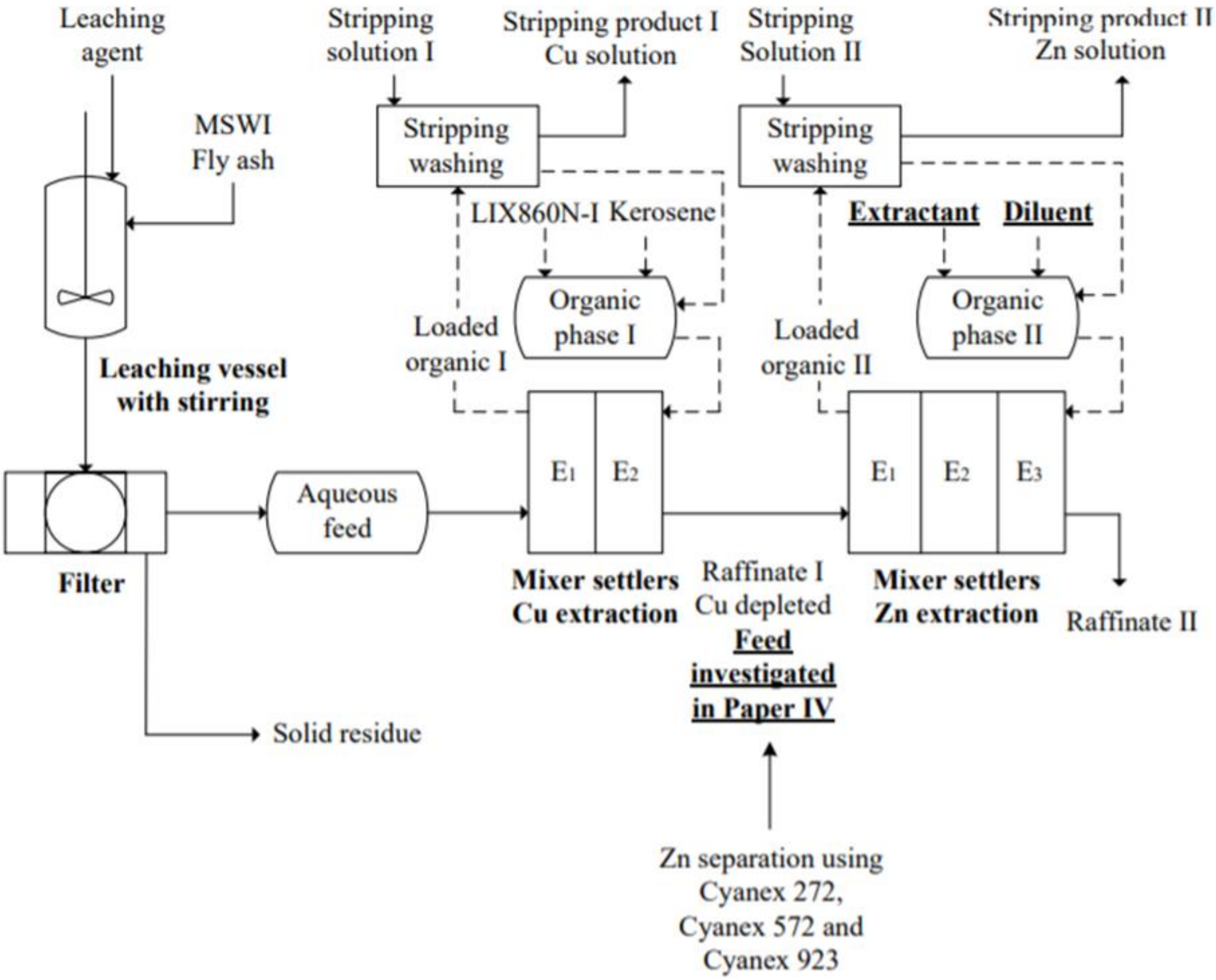
a) a value of mS / mF greater than (mS / mF) min,

b) a value of the extraction factor

$$\varepsilon = m\,p = m\,\frac{m_E}{m_R} = \text{partition coefficient } \frac{\textit{mass flow of extract}}{\textit{mass flow of raffinate}}$$

between 1,2 & 2.

2.14.5 Overview of metals recovery system



2.14.6 Cobalt[6]

Cobalt – The extraction of cobalt from hydrochloric acid using alamine 336 in *meta*-xylene.[26] Cobalt can be extracted also using Cyanex 272 {*bis*-(2,4,4-trimethylpentyl) phosphinic acid}, Marmara University

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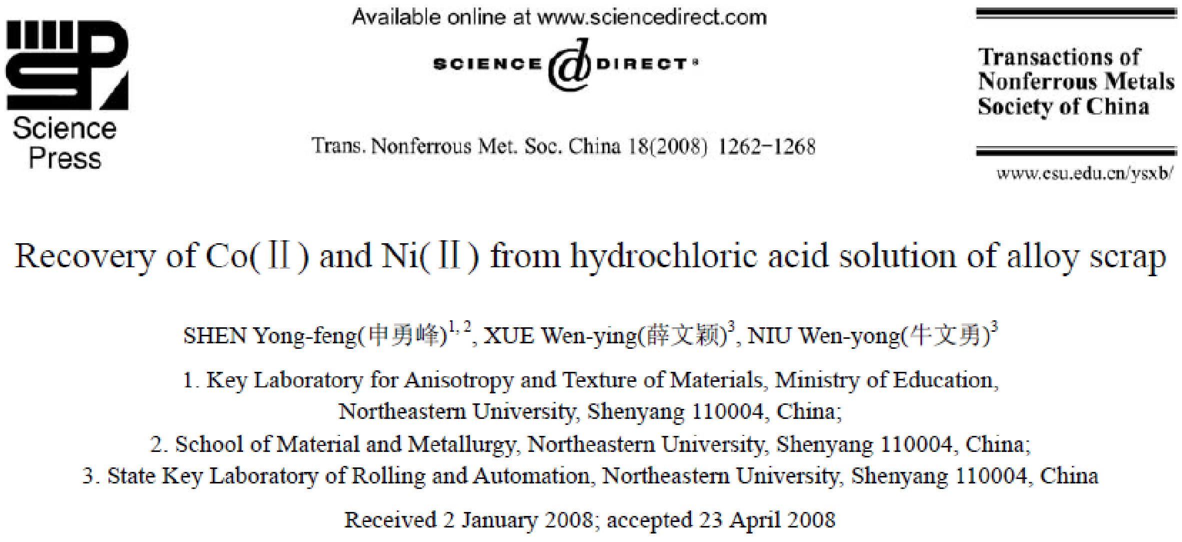
[6] Filiz, M.; Sayar, N.A.; Sayar, A.A. (2006). "Extraction of cobalt(II) from aqueous hydrochloric acid solutions into alamine 336–m-xylene mixtures". Hydrometallurgy. **81** (3-4): 167–173. doi:10.1016/j.hydromet.2005.12.007. ISSN 0304-386X.

Extraction of Co(II) from aqueous hydrochloric acid solutions into organic Alamine 336–m-xylene systems was investigated. Extraction experiments were conducted with initial metal concentrations of 1, 3 and 6 g L− 1, each at 1, 5, 8 and 10 M HCl. It was observed that the extractability of Co(II) increases with increasing acidic molarities. Alamine 336 diluted with m-xylene was found to be a suitable extractant for Co(II) for 5 to 10 M. In parallel, extractant volume-domain dynamics were investigated. A mathematical model was developed to correlate metal extractability and Alamine 336 volume content. Optimal Alamine 336 contents were estimated for single stage extraction.

Extraction of cobalt(II) from aqueous hydrochloric acid solutions into alamine... | *Request PDF*. Available from: https://www.researchgate.net/publication/229310411_Extraction_of_cobaltII_from_aqueous_hydrochloric_acid_solutions_into_alamine_336-m-xylene_mixtures [accessed Mar 25 2018].

2.14.6.1 Recovery of Co(II) and Ni(II) from hydrochloric acid solution of alloy scrap[7]



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Recovery of Co(II) and Ni(II) from hydrochloric acid solution of alloy scrap

SHEN Yong-feng(申勇峰)[1, 2], XUE Wen-ying(薛文颖)[3], NIU Wen-yong(牛文勇)[3]

1. Key Laboratory for Anisotropy and Texture of Materials, Ministry of Education,
Northeastern University, Shenyang 110004, China;
2. School of Material and Metallurgy, Northeastern University, Shenyang 110004, China;
3. State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang 110004, China

Received 2 January 2008; accepted 23 April 2008

Abstract: A hydrometallurgical process was developed for recovery of nickel and cobalt from the hydrochloric acid leaching solution of alloy scraps. The process consists of five major unit operations:

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[7] http://www.tnmsc.cn/down/upfile/soft/2008928/2008928164134995.pdf
alloy scap = legierungsschrott

1) leaching with 6 mol/L hydrochloric acid under the L/S ratio of 10:1 at 95 °C for 3 h;
2) copper replacement by iron scraps under pH value of 2.0 at 80 °C, and stirring for 1 h;
3) removal of iron and chromium by chemical precipitation: iron removal under pH value of 2.0 at 90 °C by dropwise addition of sodium chlorate and 18% sodium carbonate solution, then chromium removal under pH value of 4.0 at 70 °C by addition of nickel carbonate solution, stirred by air flow for 2 h;
4) selective separation of cobalt from nickel by extraction using 30% trialkyl amine+50% kerosene (volume fraction) and tri-*n*-butylphosphate (TBP) as a phase modifier with the O/A ratio of 2:1, and stripping of cobalt with 0.01 mol/L HCl;
5) crystallization of nickel chloride and electrodeposition of cobalt. It is found that the nickel recovery of 95% and the cobalt recovery of approximately 60% with purity over 99.9% are obtained by this process.

Key words: alloy scrap; nickel; cobalt; recovery; trialkyl amine

1 Introduction

The demand for nickel and cobalt has recently risen for their promising use in rechargeable batteries. The increase in the industrial demand for these metals has brought forth a steady growth in the need for refining of the metals. More importantly, the recovery of nickel and cobalt from secondary sources such as alloy scraps and/or spent batteries could minimize landfill disposal and the waste of natural resources. It is also technically feasible and economical in comparison with refining cobalt and nickel from ores. To date, some typical hydrometallurgical processes have been reported for the recycling of cobalt and/or nickel from lithium ion batteries[1−3] and nickel metal hydroxide batteries[4−7] as well as Ni-Cd batteries[8]. These hydrometallurgical routes consist of acid leaching, separation of cobalt from nickel and/or lithium, and recovery as chemicals. For example, nickel has been recovered by means of both galvanostatic and potentiostatic electrowinning after separating Ni from Co by SX methods[9]. In addition, the recovery of Co(II) and Ni(II) from different sources, including polymetallic sea nodules[10−11], cobalt enriched Ni-Cu matte [12], low-grade sulfide flotation concentrates[13] and low-grade Ni-Cu sulfide tailings [14], has been achieved by different research groups.

However, there have been only a handful of published works on cobalt recovery from waste alloys[15]. A variety of organic solvents or their mixtures have been tested for the extraction of nickel(II) and cobalt(II) from aqueous solutions and for separation of cobalt from nickel. Among the acidic organo-phosphoric compounds, di(2-ethylhexyl) phosphoric acid (D2EHPA) and extractant 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA, commercially known as PC88A or P507), have been widely used for separation of Co from Ni [11−1 6].

Whereas organo-phosphorous acid derivatives such as bis(2, 4, 4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) extractant can extract cobalt and nickel at very low pH value as well as the ability to reject metals such as calcium, manganese and magnesium, holding a position for separation of cobalt and nickel[17−18]. The investigation on the purification of nickel showed that di-2, 4, 4-trimethylpentyl phosphinic (Cyanex 272) was most effective for selecting

2.15 Fly ashes treatment

The presence of heavy metals in municipal solid waste incineration (MSWI) fly ash is of environmental concern due to their leaching potential in landfill environments. Acid extraction is a conventional method of safe treatment of fly ash. In this work, nitric acid was used as the extraction acid to leach Ni, Zn, Pb and Cu out from the ash. In addition, influence of nitric acid concentration and liquid to solid ratio on removal ratio of the four heavy metals was studied. It was found that removal ratio followed the decreasing sequence of Pb > Cd > Cu > Zn for acid extraction using nitric acid. The optimal extraction condition was 5.3 mol/L of nitric concentration at 20 liquid to solid ratio, which resulted in a removal ratio of 98% for Pb, 86% for Cd, around 73% for Cu and around 42% for Zn.[8]

2.16 LANDFILL GAS (Methane gas from waste)[9]

Created during the decomposition of organic substances, landfill gas consists of methane, carbon dioxide, and nitrogen. The controlled collection and combustion of this problem gas is an indispensable step in the modern operation and re-cultivation of a landfill site. In addition, the high calorific value of landfill gas makes it a viable fuel for gas engines that can be effectively used for power generation. With more than 25 years of experience in the combustion of landfill gas throughout the world, GE’s Jenbacher gas engines provide an excellent solution for using your waste gas as an energy source.

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[8] H. Y. Zhang and G. X. Ma, "Leaching of Heavy Metals from Municipal Solid Waste Incineration (MSWI) Fly Ash Using Nitric Acid", Applied Mechanics and Materials, Vols. 249-250, pp. 918-921, 2013

[9] https://www.gepower.com/applications/waste-gas-to-power

2.17 Methane liquefaction

EP 2 251 625 A2
EUROPEAN PATENT APPLICATION

Pre-cooled liquefaction process of natural gas

2.17.1 LNG Proprieties

LNG has the best safety record of all fossil fuels: Not flammable or explosive in liquid form

Noncorrosive and nontoxic

Stable and stored at low pressures

Evaporates quickly and completely leaving no fire hazard puddle

LNG is refrigerated around -160˚C

Volume reduction 600 times with the same calorific capacity

LNG is composed mainly from methane (more than 90%)

The liquefaction factory consumes nearly 10% of the natural gas while functioning

The LNG will be stocked at an atmospheric pressure in storages made from concrete or metallic tanks, possessing double wall and thermal insulation.

The principals LNG exporters are: Qatar, Australia, Malesia, Nigeria and Indonesia (more than two-thirds)

The principals LNG importers are: Japan, South Korea, China.

2.17.2 The process of producing LNG is in three steps.

Feed gas from the interior	
Step 1- Treatment (Remove CO2, Water (H2O) and mercury from the Feed Gas)	Acid gas (mainly carbon dioxide), water and mercury are removed from the gas delivered to Oman LNG. This clean-up” is a necessary step to enable liquefaction of the natural gas and a safe product for our customers.
Step 2 – Removal of “Condensates”(Remove heavier hydrocarbons (NGL’s) by Fractional Distillation)	**Condensates (natural gas Liquids made up mainly of pentane and hexane) are removed by Fractional Distillation of the feed Gas after treatment.**
Step 3 – Liquefaction of Natural Gas(Cool remaining light hydrocarbons to-162ºC to liquefy)	The gas (now mainly methane) is sent to the Main Cryogenic Heat Exchange (MCHE), where it condenses to liquid at -162°C. The liquid is sent to special storage tanks awaiting shipment by LNG vessels to customers in Asia and Europe.

2.17.3 LNG Production diagram

US5053209A

FIG. 1

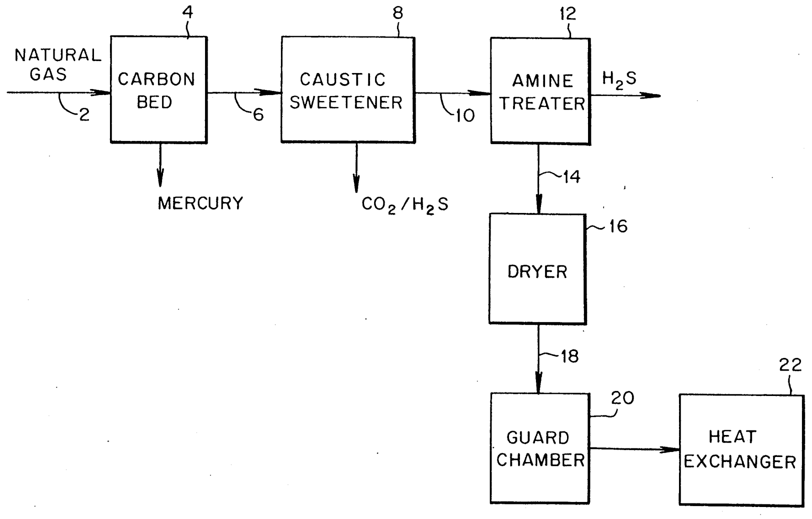
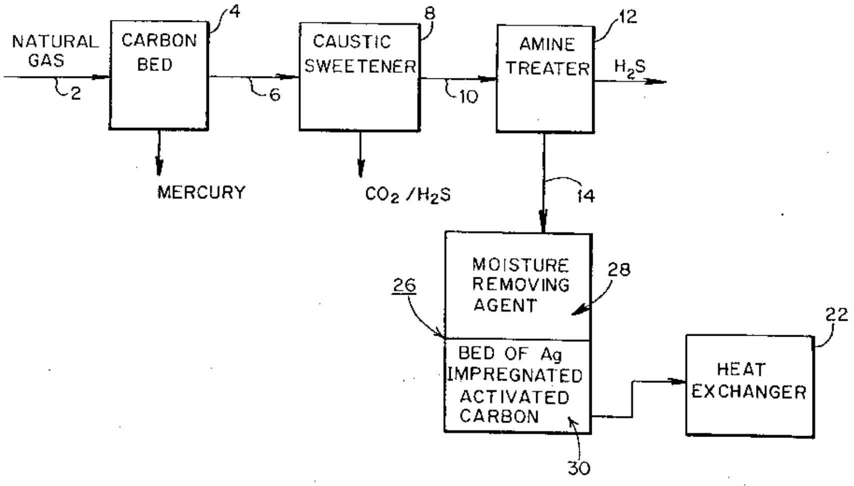


FIG. 2



SUMMARY OF THE INVENTION

In a broad sense this invention comprises a process for treating raw natural gas prior to liquefaction which comprises (a) passing a stream of raw natural hydrocarbon gas or liquid through a zone containing activated carbon impregnated with sulfur, at conditions effective to remove mercury from said natural gas; (b) passing the effluent stream of natural gas thus treated through a sweetening zone operating at conditions effective to remove carbon dioxide and hydrogen sulfide and/or then passing the effluent stream through an amine treating system where additional hydrogen sulfide is removed, (c) subsequently passing the effluent through a drier or dehydrator where water vapor is removed and (d) finally passing the effluent through a heat exchanger to a further product treatment zone. In this invention there is positioned in the flow line, preferably downstream of the dehydrator, or dryer, a body of activated carbon, silica, alumina, or silica-alumina supports, which can be honeycomb shaped, extrudate, granules, beads, and pellets containing free silver in an active state such that it forms an amalgam with mercury. The silver preferably is deposited in a dispersed form on activated carbon, or even more preferably on gamma alumina, although other supports can be used such as silica, other aluminas such as alpha or beta, and silica-alumina. This technique is particularly useful in removing the residual mercury still remaining in the gas stream even after it has been treated under optimum operating conditions by equipment located upstream.

2.17.4 Natural Gas Treatment

2.17.4.1 Step1: Mercury removal

DETAILED DESCRIPTION OF THE INVENTION

In the prior art the most popular absorbent used to remove mercury is sulfur loaded on activated carbon. The reaction between the sulfur and mercury is:

2Hg+S.sub.2 →2HgS

The optimum operating temperature has been determined to be about 170° F.

The substrate utilized in the method of this invention is metallic silver dispersed preferably on activated carbon or on gamma alumina. Other usable support materials include other types of alumina, silica, silica-alumina, silicates, aluminates and silica aluminates, as well as synthetic and natural zeolites, to increase the metal surface area to greater than $0.01m_2$ /g to improve activity for mercury removal. The concentration of silver metal on the activated carbon or gamma alumina should be between 0.1 and 20 percent by weight (preferably between 1 and 5 percent). The silver can be dispersed onto the carrier by impregnation, co-precipitation or other well-known methods. The absorbent can be in the form of extrudate, beads, pellets and granules. Pressure drop across a body of absorbent can be minimized by using absorbent in the form of honeycomb, or "multi-lobe" configuration.

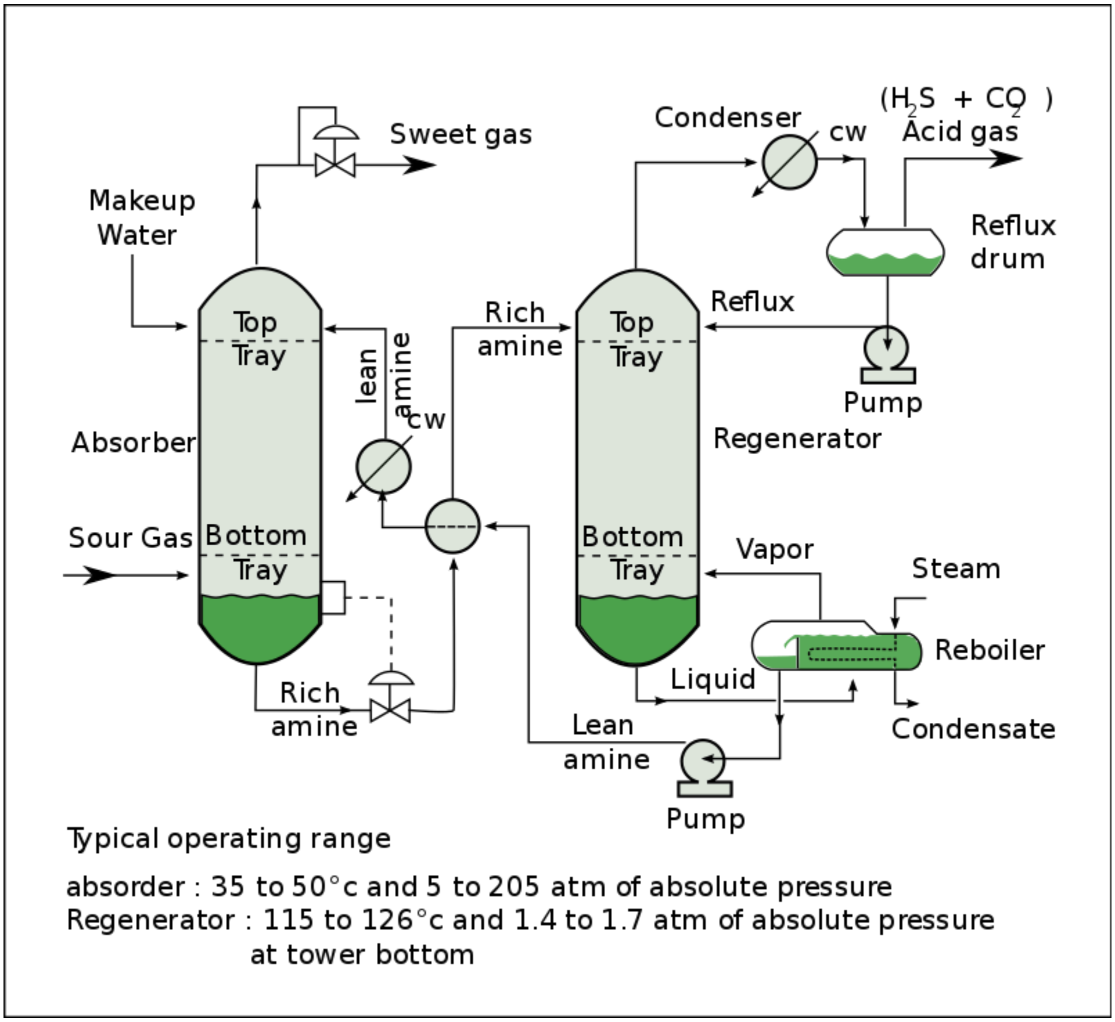
EXAMPLE

An adsorbent consisting of silver deposited on gamma alumina was prepared by saturating the gamma alumina with an aqueous solution of silver nitrate, drying and calcining the impregnated alumina, and then reducing the silver nitrate to free metallic silver by contacting the alumina with formaldehyde. The adsorbent contained approximately 5 percent by weight of silver. An initial test of the adsorbent in which 0.1 gram of the adsorbent was contacted with 100 milliliters of air equilibrated with mercury indicated that 98 percent of the mercury in the air was removed.

2.17.4.2 Step2: Treatment CO2 removal

Amine Units

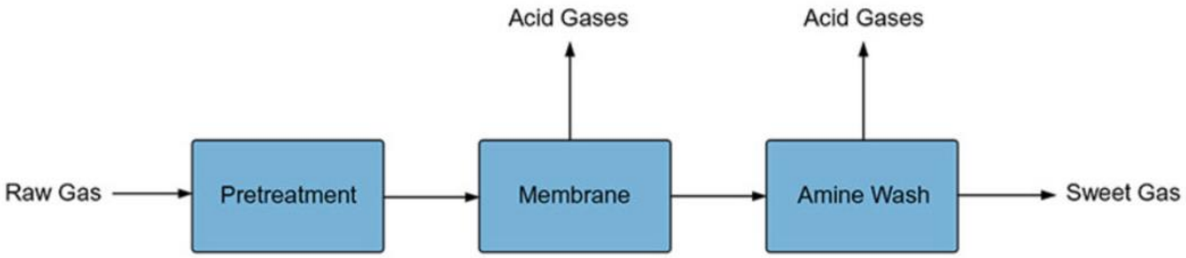
Amine-based solvents are an effective method for processing acid gas, from natural gas, associated gases or unconventional gas sources which have varying compositions of hydrogen sulfide and carbon dioxide. Depending on the composition of raw gas, we implement formulated or generic amine based solvents for an optimal selective processing plant.



Acid Gas Removal Amine Wash

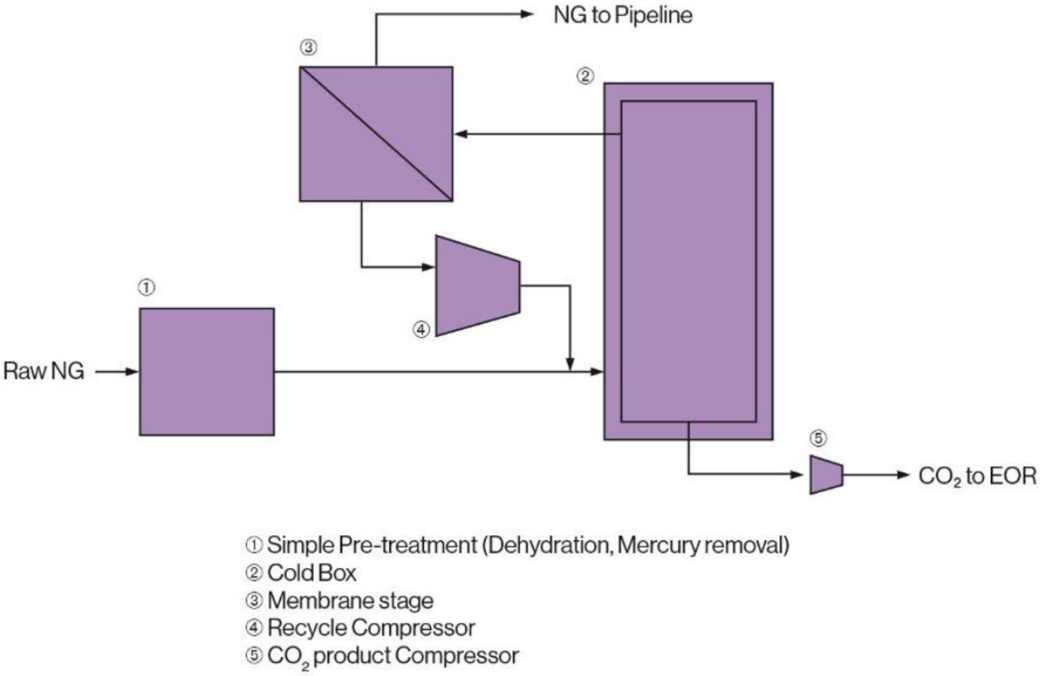
Membrane Technology

In case of carbon dioxide rich gas, meeting product specifications requests a particularly efficient method of removing carbon dioxide. In collaboration with Air Liquide Advanced Separations/Porogen, Air Liquide Engineering & Construction offers hollow fiber membrane technology for selective permeation of carbon dioxide while minimizing hydrocarbon losses. This technology combines high permeability with high hydrocarbon resistance, making it an attractive option for bulk carbon dioxide removal. In addition, the operation is highly flexible, it requires little maintenance, making it ideal for remote and offshore locations



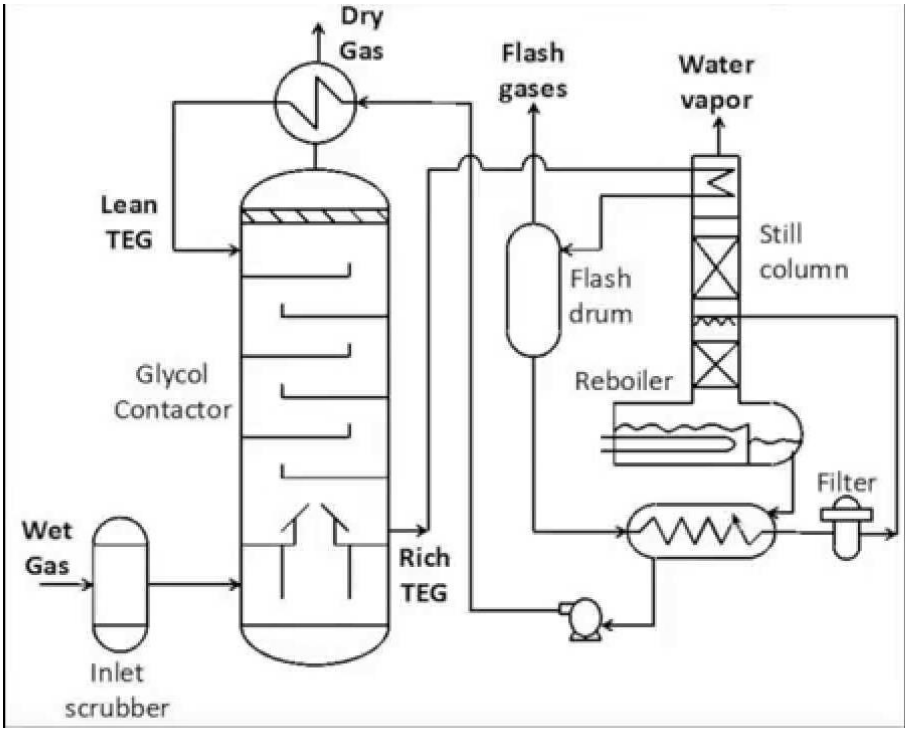
Cryogenic technology

For natural gas with high CO_2 content, Cryogenic technology, alone or in combination with the Air Liquide membrane technology, can produce pipeline specification natural gas. High CO_2 partial pressure favors the partial CO_2 condensation and making its separation from natural gas even easier. The CO_2 and heavy hydrocarbons condense in the cold box and are collected at high pressure. This Air Liquide Engineering & Construction proprietary technology also allows Natural Gas Liquids recovery with almost no additional cost.



CO2 Removal Cryocap

Step 3: Water removal (Glycol dehydration)



The wet gas enters the inlet scrubber to remove solid particles. Then it will pass to the glycol contactor. In the contactor the flow of wet NG will meet with the lean Triethylene glycol (TEG). During the contact in the contactor the TEG will be invested by water and flows out of the bottom out of the contactor. The Rich TEG continue to the internal heat exchanger which is incorporated at the top of the still column in the regeneration section of the adsorption unit then it flows to the flash drum where the flash gases are released and separated from the stream. The TEG then runs to the cold side of the TEG-TEG heat exchanger. Just afterwards, the warm TEG is filtered then runs into the regeneration system where it's spread in the still column. From there the TEG runs into the reboiler. The regeneration energy is around 282 kj/L of TEG, the temperature should not exceed the decomposition temperature of the TEG. The regenerated TEG is pumped to the hot side of the TEG-TEG heat exchanger and the NG-TEG heat exchanger at the top of the contactor.

2.17.5 Pre-cooled liquefaction process of natural gas

FIGURE 1

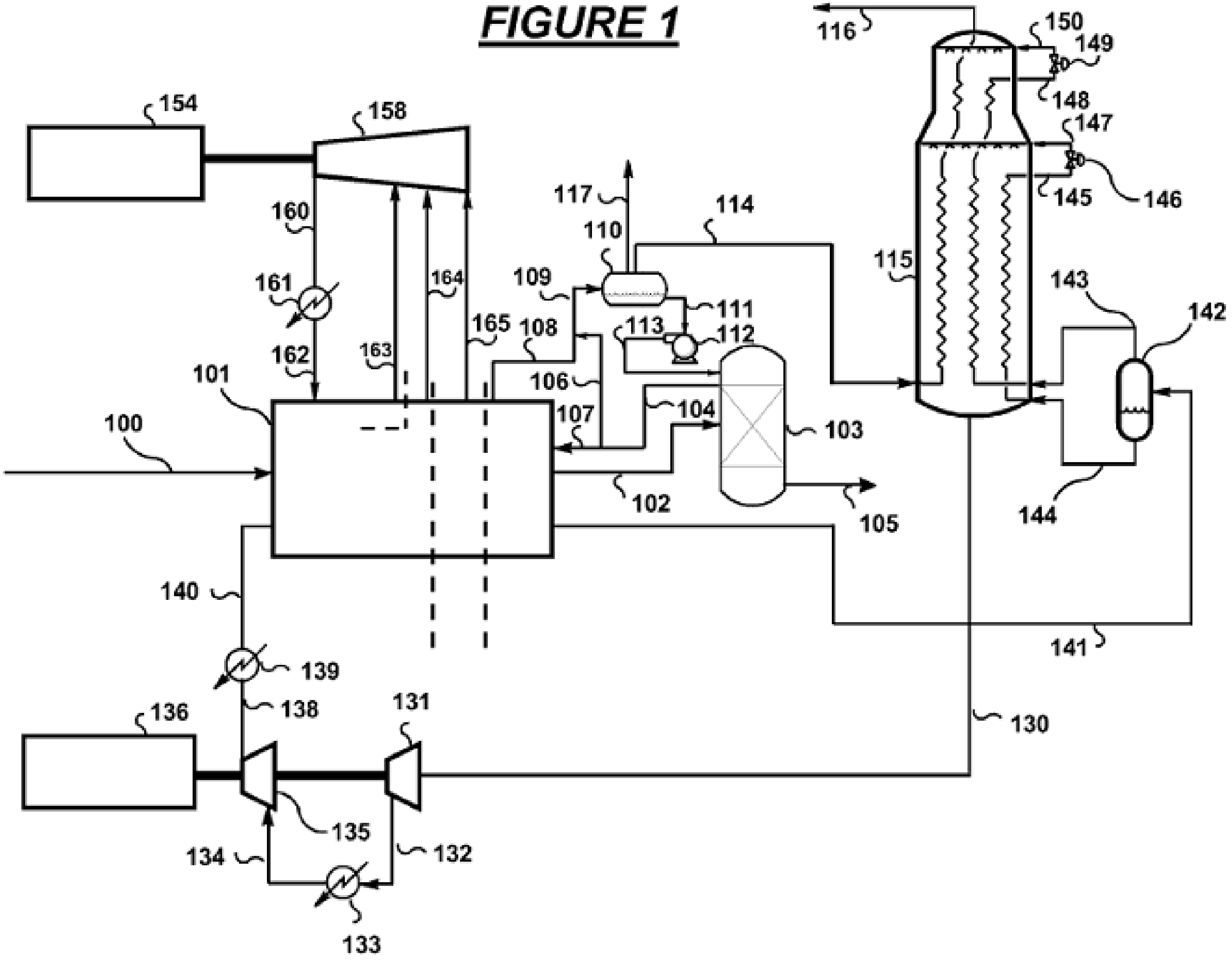


FIGURE 1

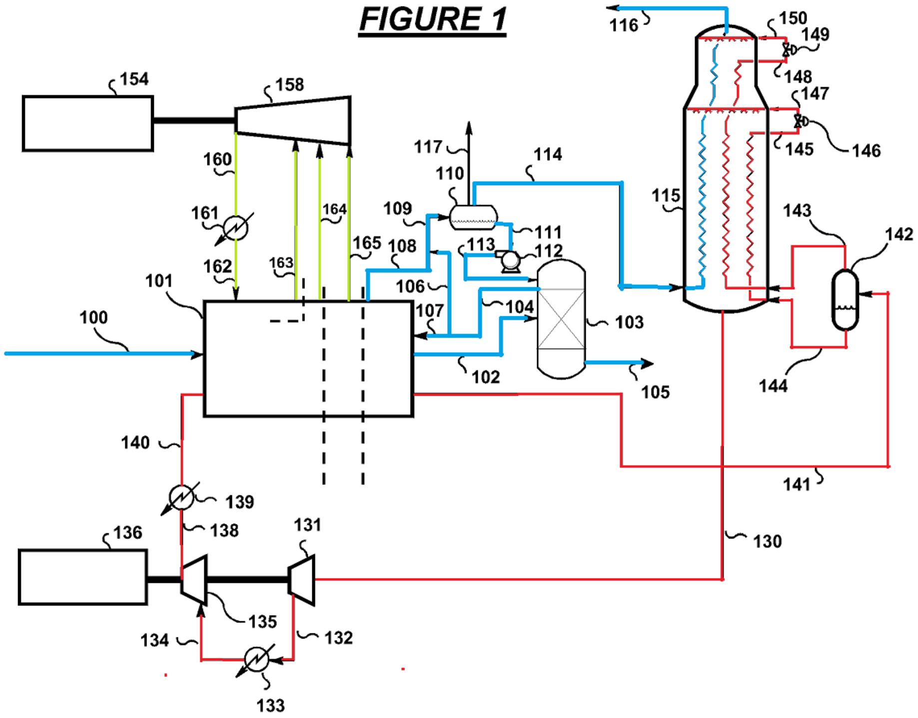
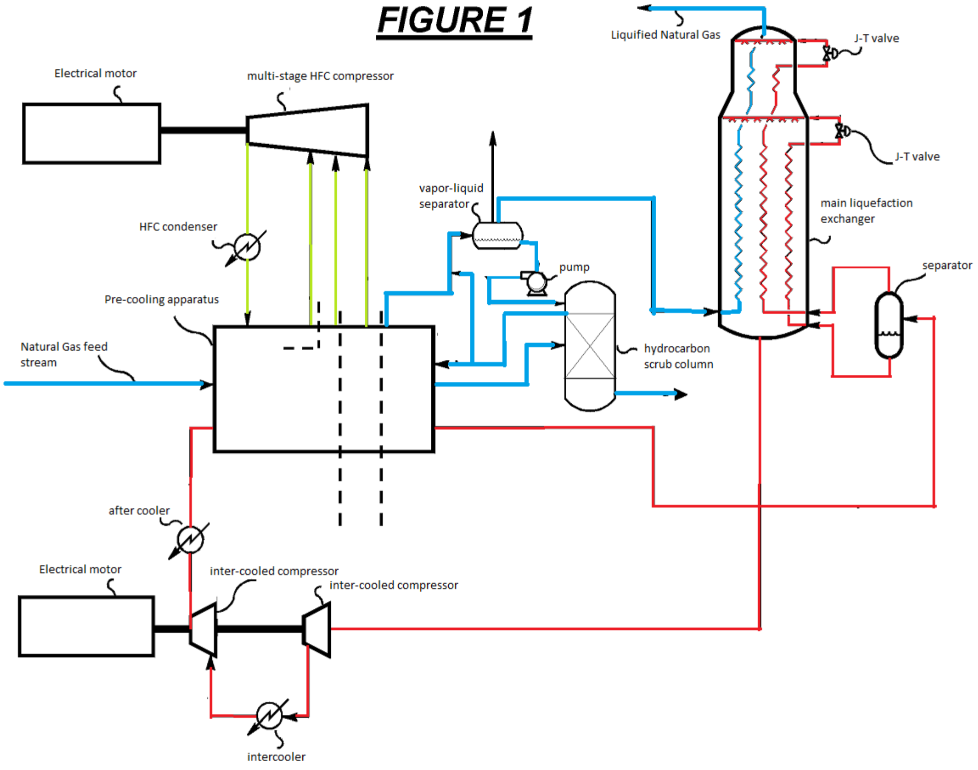


FIGURE 1



100: natural gas feed stream

101: pre-cooling apparatus

102: pre-cooled stream

103: hydrocarbon scrub column

104: stream

105: heavy hydrocarbon stream

106,107: stream

108: partially condensed feed stream

109: stream

110: vapor-liquid separator

111: liquid stream

112: pump

113: cold liquid reflux stream

114: vapor stream

115: the main liquefaction exchanger

116: stream

117: methane make-up stream

130: low pressure, warm main liquefaction refrigerant stream

131, 135: inter-cooled compressors

132, 134, 138: stream

133: intercooler

136: driver (electrical motor or gas turbine)

139: after cooler

140: high pressure fluid stream (P: 30-80 bara)

141: pre-cooled stream

142: separator

143: lighter refrigerant stream

144: heavier refrigerant stream

145: stream

146, 149: J-T valve

147,150: cryogenic refrigerant stream

148: stream

154: multi-shaft gas turbine

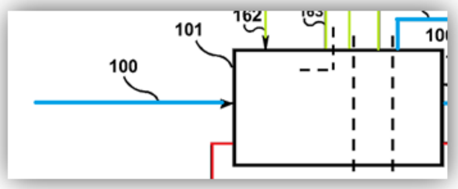
158: multi-stage HFC compressor

160: stream

161: HFC condenser

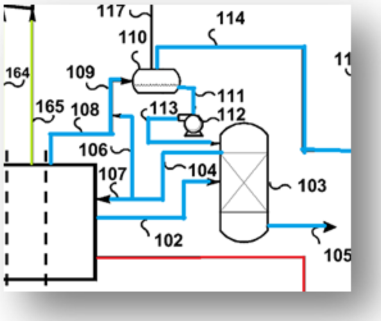
162: sub-cooled HFC stream

163, 164, 165: combined stream



Description:

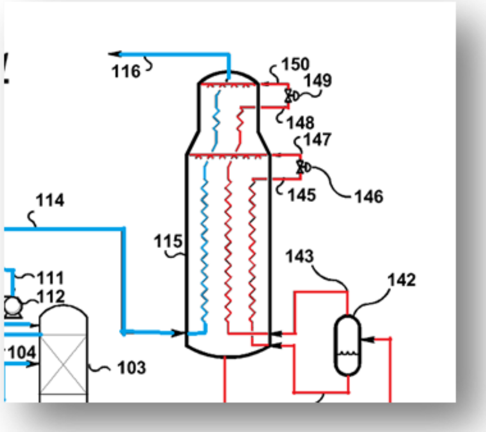
<u>Step 1:</u> Returning to Figure 1, a natural gas feed stream (not shown) is pre-treated for removal of heavy hydrocarbon oils, particulates, CO2, and H2S before being sent to driers (not shown). Drying may be performed using sea water cooling if the sea water is substantially below 22°C or can be performed using the HFC refrigerant. After cooling the natural gas feed stream to a temperature between 22-25°C, the natural gas feed stream is then sent to drier beds where moisture is removed (not shown). The dehydrated natural gas feed stream 100 is then sent to be pre-cooled at pressures ranging between 30-85 bara. Pre-cooling of dehydrated natural gas feed stream 100 is performed in 1-5 cooling stages in series, for example, represented by the pre-cooling apparatus 101. Figure 1 illustrates a 3-stage pre-cooling system. These serial cooling stages use an HFC refrigerant at sequentially descending temperatures by lowering J-T valve pressures making the HFC refrigerant supplied to the cooling stage (n) colder than that supplied to the cooling stage (n-1), for example. The greater the number of cooling stages, the greater the efficiency of pre-cooling due to close approaches of the cooling curve. If there are a total of (n) HFC pre-cooling stages, then the feed cools in (n-1) stages to yield the pre-cooled stream 102.



<u>Step2:</u> Pre-cooled stream 102 may then be sent to a hydrocarbon scrub column 103 which scrubs away heavier (C3+) components of the feed using a cold liquid reflux stream 113 in order to adjust the heating value of the final LNG. A bottoms stream 105 is sent either to a fractionation train or to storage (not shown). It should be noted that due to space constraints on FPSOs, the heavy hydrocarbon stream 105 exiting the scrub column 103 may be potentially shipped and fractionated at a LNG receiving terminal. If fractionation is undertaken on the FPSO platform, one aspect of the current invention also allows for the HFC refrigerant to supply refrigeration to condensers of the various columns (such as a deethanizer) that may be involved in a fractionation train.

<u>Step 3:</u> Stream 104, taken from the scrub column 103, constitutes the lighter overhead stream. Part of stream 104 (i.e., stream 107) may be partially condensed using the HFC pre-cooling apparatus 101. The partially condensed feed stream 108 may then be combined with the uncondensed portion of stream 104 (i.e., stream 106) to form stream 109 and then sent to a vapor-liquid separator 110 which disengages the vapor from the liquid. The liquid stream 111 from the vapor-liquid separator 110 may then be pumped in pump 112 back into scrub column 103 as stream 113 to act as the column reflux.

<u>Step 4:</u> The HFC pre-cooling refrigerant may be used to supply all of the scrub column reflux condenser 110 duty without the need to use the main liquefaction refrigerant for such purpose. Using the HFC pre-cooling to supply all of the scrub column reflux condenser 110 duty will improve the efficiency of the system since typically cooling duties supplied by the typical hydrocarbon refrigerants require much higher incremental compression power than the HFC refrigerant. This is because of the significantly lower compressibility factors of typical HFC's when compared with lighter hydrocarbon refrigerants like CH_4 and C_2H_6. Use of the HFC pre-cooling to supply all of the scrub column reflux condenser 110 duty also reduces the size of the main liquefaction exchanger 115 and simplifies control issues and plant layout.

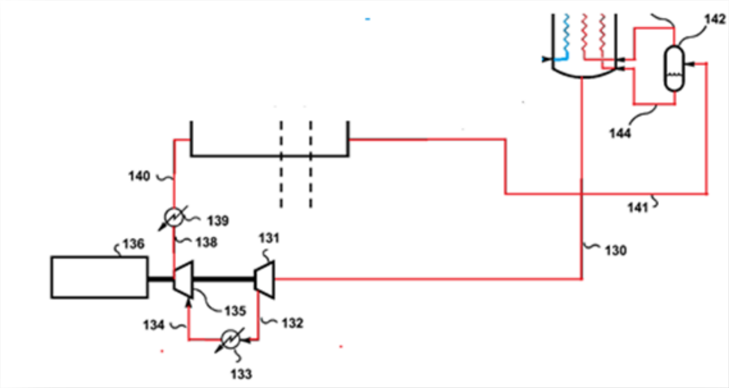


Step 5: Vapor stream 114 from the scrub column reflux condenser 110 may be sent to the cryogenic section of the plant that fully condenses and sub-cools vapor stream 114 to form LNG product stream 116. The cryogenic section comprises the main liquefaction exchanger 115. In the cryogenic section, either a refrigerant consisting of mixed hydrocarbons with 0-30 mole% N2 or pure N2 may be used, for example. In one embodiment, the main liquefaction refrigerant may be a mixture containing 0-30% N2 and hydrocarbons such as methane (0-50%), ethane (0-75%), and butanes (0-50%). In another embodiment, the main liquefaction refrigerant may be a mixture comprising a first stream of methane derived from a natural gas stream, a second stream, where the second stream is an ethane enriched stream that is predominantly ethane, and a third stream, where the third stream is a nitrogen enriched stream that is predominantly nitrogen. The methane stream can be derived from natural gas in one of two ways. If natural gas stream 100 (illustrated in Figure 1) is lean (i.e., contains more than 90 mole % methane and less than 3 mole % propane) then a part of that stream may be used to make up the mixed refrigerant. If natural gas stream 100 (of Figure 1) is not lean (i.e., contains more than 3 mole % propane) then it may be pre-cooled against the HFC in pre-cooling apparatus 101, scrubbed in a scrub column 103 (of Figure 1) that removes excess propane and other heavier hydrocarbons, and pre-cooled further to produce the methane make up stream 117 (of Figure 1). This procedure ensures that the methane make up stream used to make the mixed refrigerant contains low enough amounts of propane for safety.

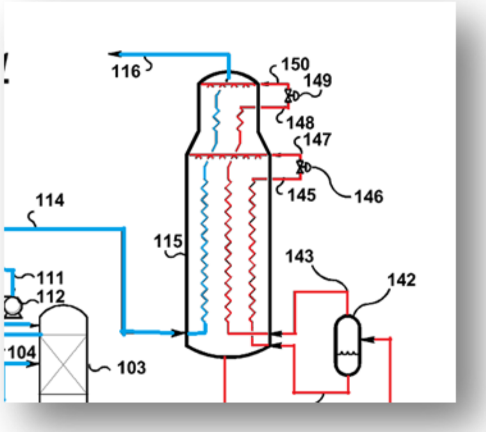
The use of propane, which is considered to be unfavorable for use on the FPSO due to the possibility of formation of flammable clouds at surface level, may be eliminated, or nearly eliminated when using HFC's as a pre-working fluid.

Step 6: The main liquefaction exchanger 115 may be a wound coil exchanger, a plate-fin exchanger, or any other exchanger typical for cryogenic service. Vapor stream 114 may enter the main liquefaction exchanger 115 where it is condensed and sub-cooled and exits as LNG product stream 116 at a temperature between -140°C to -170°C and pressure between 30-85 bara, for example.

Step 7: The condensed and sub-cooled LNG product stream 116 may be further processed by reducing its pressure in a liquid expander (not shown) or a flash valve (not shown) to around 1.2 bara, forming flash gas and a liquid LNG product. The LNG product may be subsequently sent to storage, for example.



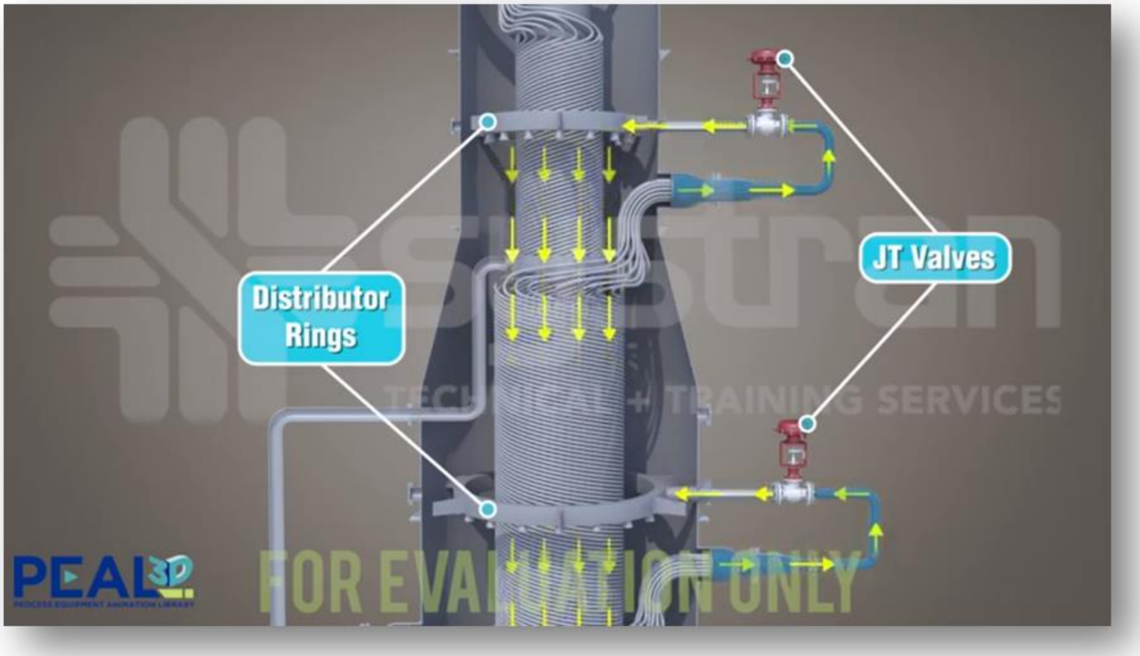
Step 8: The low pressure, warm main liquefaction refrigerant stream 130 may be sent to a sequence of inter-cooled compressors 131, 135 where the stream 130 is first compressed in compressor 131 to form stream 132, cooled in intercooler 133 to form stream 134, further compressed in compressor 135 to form stream 138, and then further cooled in aftercooler 139 to emerge as a high pressure fluid stream 140. Compressors 131 and 135 are driven by driver 136. Driver 136 can be an electrical motor or a gas turbine. High pressure fluid stream 140 may be at pressures ranging between 30-80 bara and a temperature dictated by: (1) the working fluid used in the intercooler 133 and aftercooler 139; and (2) the size of the intercooler 133 and aftercooler 139. While Figure 1 illustrates the mixed refrigerant compression system having one intercooler 133 and one aftercooler 139, multiple intercoolers and aftercoolers may be implemented, for example. The working fluid used in the intercooler 133 and aftercooler 139 may be air, or typically for FPSO applications, sea water, or fresh water, which is in turn cooled by sea water, for example.



Step 9: The cooled high pressure refrigerant stream 140 may be pre-cooled using pre-cooling apparatus 101 resulting in pre-cooled stream 141. Pre-cooled stream 141 may be separated into lighter refrigerant stream 143 and heavier refrigerant stream 144 in separator 142. The lighter refrigerant stream 143 may then be condensed and sub-cooled in the main liquefaction exchanger 115 to form stream 148, expanded in J-T valve 149 to generate cryogenic refrigerant stream 150 having a temperature between -180°C to -120°C, before it is then vaporized in the main liquefaction exchanger 115. The heavier refrigerant liquid stream 144 may also be sub-cooled in the main liquefaction exchanger 115 to form stream 145 where it may then be expanded in J-T valve 146 to generate cryogenic refrigerant stream 147 to also be vaporized in the main liquefaction exchanger 115. The current process may also include a hydraulic expander (not shown) before J-T valve 146 to improve efficiency.

The combined cryogenic refrigerant streams 147, 150 boil at successively higher temperatures while flowing down the main liquefaction exchanger 115 before eventually exiting the exchanger as the vapor stream 130 at or slightly above dew point thereby completing the refrigeration loop.

MCHE: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PROCESS EQUIPMENT ANIMATION LIBRARY

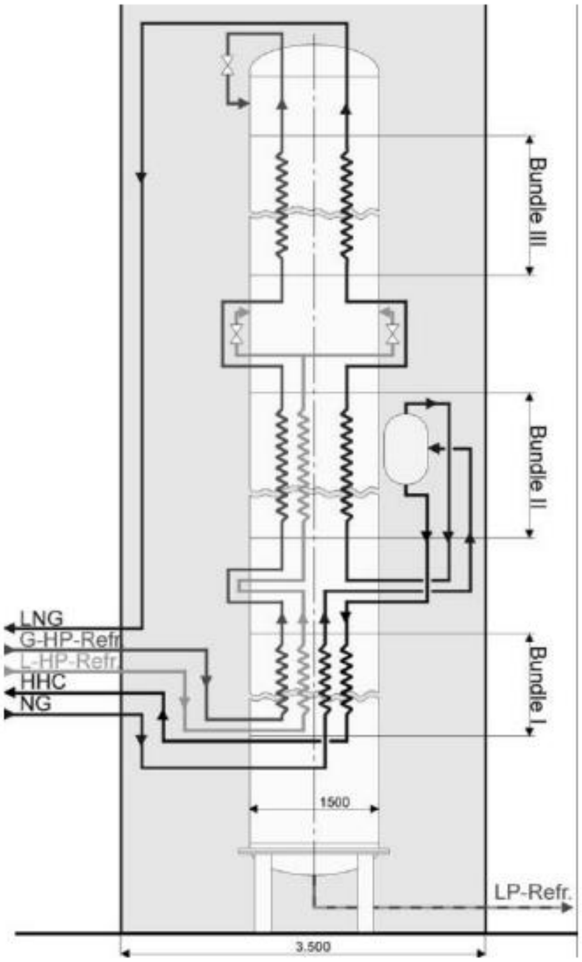

PEAL 3D
PROCESS EQUIPMENT ANIMATION LIBRARY

The MCHE is a spiral wound heat exchanger consisting of bundles with thousands of tubes to provide sufficient surface area needed for a close temperature approach between the inlet gas and the cooling medium. These bundles can be classified as warm and cold bundles and are arranged in a vertical shell with the warm bundle on the bottom and the cold on top.

The high pressure mixed refrigerant is first cooled by propane and is subsequently separated into light and heavy mixed refrigerant streams. The high pressure mixed refrigerant and feed gas streams flow upward through the tube side of the MCHE while the high pressure mixed refrigerant undergoes a series of flashes dramatically reducing the temperature. The cold flashed mixed refrigerant flows counter current (shell side) to cool both the inlet gas and the inlet mixed refrigerant. A final cooling stage is accomplished through a J-T valve or hydraulic expander to further cool the liquid and remove any excess nitrogen. At this stage, the gas stream is fully liquefied to -160°C, and is pumped to storage. The warm vaporized MR stream is taken off the bottom (shell side) of the exchanger and enters the first stage suction of the MR compressor. The compressed MR is first cooled with air or water followed by propane before returning to the MCHE to repeat the process.

Thermal Design

A Spiral wound heat exchangers (SWHEs) is generally used in LNG plant.



Cold Box Bundle Arrangement

(gaseous high pressure refrigerant (G-HP-Refr.))

As to suit process requirements three bundles are arranged in series, installed in a common shell. Each bundle has a diameter of 1,325 mm and the total installed heating surface amounts to 3,900 m^2. Bundle no. 1 is used to liquefy heavy hydrocarbons of the natural gas stream. Bundle no. 2 leads to partial liquefaction and in bundle no. 3 total liquefaction and sub-cooling to around –162°C are achieved. Each bundle has a separate distribution system for the shell side MRC.

Mechanical Design

All parts of the exchanger are in aluminum alloys whereby particular care was taken to select the appropriate alloys for critical items. Design pressure for the shell side is 28 barg due to overall plant conditions and for the tube sides 48 barg. Design temperature is +55 / -175°C.

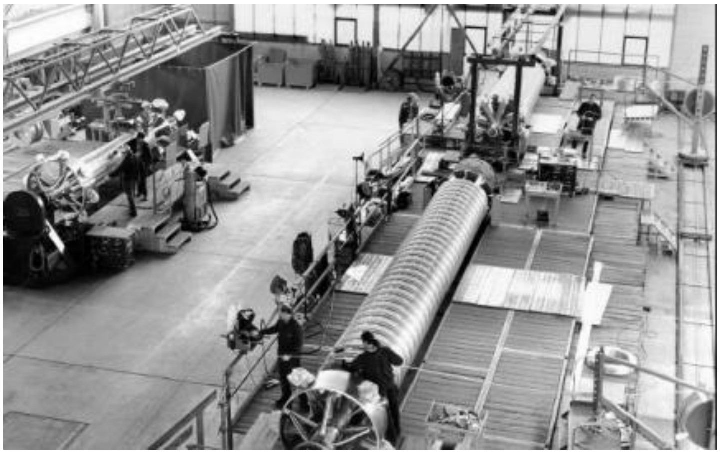
The SWHE is designed in such a way that each of the three tube bundles has its own mandrel, support star, distributor system and shroud. Each bundle is hanging freely on several support arms via special shaped support bars so that shrinkage and expansion of the tube bundle due to rapid temperature changes during start-up or shut-down occurs with a minimum of stress between tube bundle and shell.

Each tube bundle is to be wrapped into a shroud which is seal-welded on the upper side to the shell to avoid any by-pass of refrigerant between bundle and shell.

The bottom section of the SWHE is designed so that it can be used as a separator. As the SWHE had to be installed in a cold box all bonnets and nozzles had to be designed for adequate elevation and orientation in particular in view of interconnecting piping and wall penetrations. The cold box was designed to accommodate the SWHE with a diameter of 1,500 mm and a total height of 28,600 mm including separator, all interconnecting piping, control valves, drains, vents and all instrumentation.

Manufacturing

First the mandrels with support arms and the drilled tube sheets placed in their final position were fabricated and assembled.



Three Bundles during Winding

Then the tubes were wound helically on the mandrel with a constant pitch and the winding direction being changed at each layer. Spacer bars were installed between each layer to provide the required spacing. Each tube was wound individually as to ensure proper line-up of the tubes. Particular attention was paid to keeping unsupported length of tubes between bundle and tube sheet within given limits. The bundle winding was performed in parallel on three winding benches. The tube ends on the tube sheets were then prepared for welding. A special welding process was developed for this rather critical welding seam and applied with excellent results.

After the three tube bundles had been wrapped into shrouds they were assembled with the prefabricated shell sections and completed to one exchanger. As soon as the pneumatic pressure tests on shell and tube sides had been carried out, the SWHE was installed in the cold box.

Prefabricated pipe sections were connected to exchanger, separator and valves. The instrumentation was installed followed by an additional pneumatic pressure test for all systems. Finally, the completed cold box was sealed and prepared for transport.

SWHE Installation into Cold Box

The SWHE Cold Box

OPERATION AND PERFORMANCE

To demonstrate and prove the thermodynamic and hydraulic design as well as the mechanical integrity the exchangers are equipped with a large number of flow -, temperature -, pressure - and pressure difference indicators. As a special feature about 30 calibrated temperature indicators are installed in the three bundles to compare predicted with actual temperature profiles of the SWHE. These temperature indicators provided a complete detailed picture of the temperature profiles of each bundle.

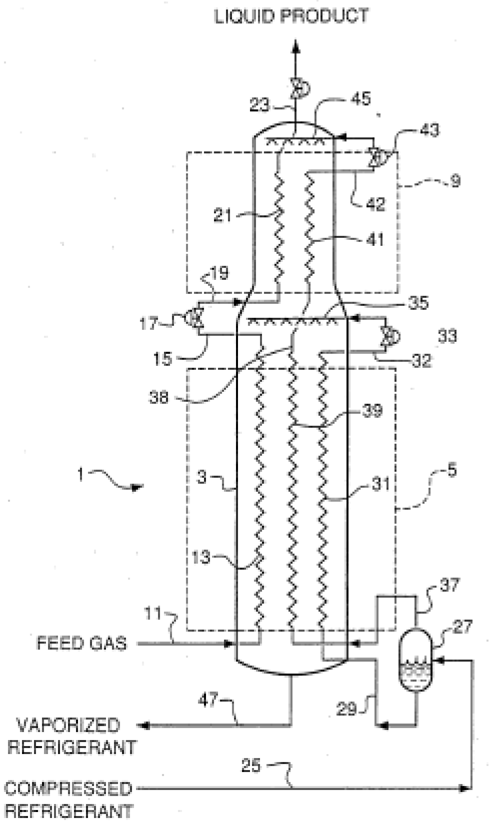
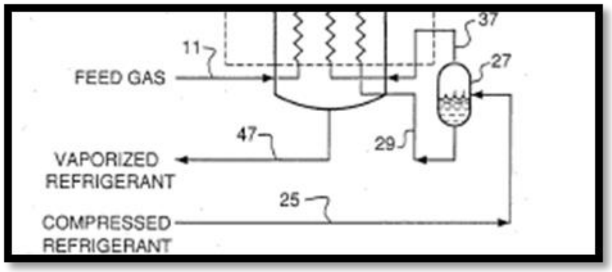


FIG. 1
PRIOR ART

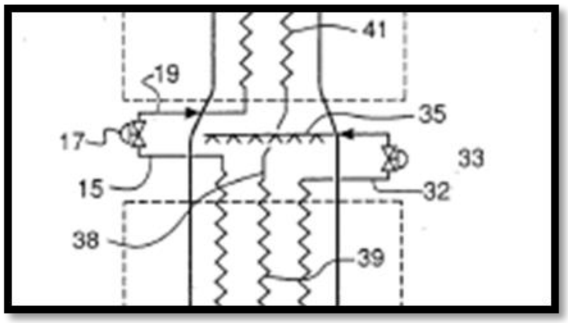
A main heat exchanger of a type known in the natural gas liquefaction field is shown in the schematic drawing of Fig. 1. This particular exchanger utilizes two coil wound bundles for the final cooling and liquefaction of a pretreated natural gas feed.

Step1: Main heat exchanger 1 comprises pressure vessel 3, warm heat exchange zone 5, and cold heat exchange zone 9. A first coil wound heat exchanger bundle is utilized in cold heat exchange zone 5 in which a feed gas provided in line 11 is initially cooled in tube circuit 13 against a vaporizing refrigerant (later described) on the shell side of the bundle. Tube circuit 13 represents multiple tubes which are part of a coil wound bundle, wherein the bundle also includes tube circuits 31 and 39 as described later. Tubes typically may be made of aluminum. Feed gas in line 15 which has been cooled and at least partially condensed optionally is reduced in pressure across throttling valve 17.

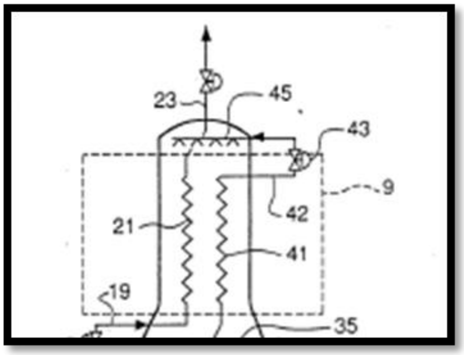
The reduced-pressure feed then flows via line 19 into tube circuit 21 in cold heat exchange zone 9, wherein the feed is further cooled and withdrawn as product via line 23.



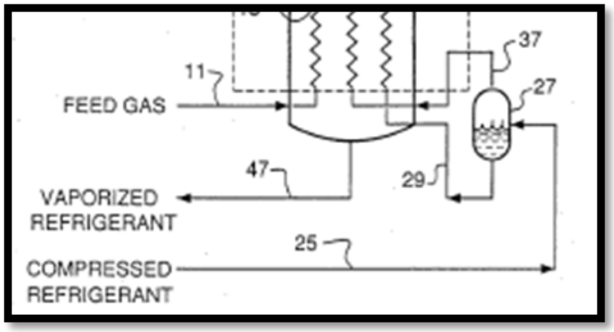
Step2: A two-phase compressed refrigerant, typically a multicomponent refrigerant containing light hydrocarbons and optionally nitrogen, is supplied via line 25 from a refrigerant compression system (not shown) and flows into phase separator 27. Refrigerant liquid is withdrawn via line 29, subcooled in tube circuit 31, and reduced in pressure across throttling valve 33. Optionally, a hydraulic expansion turbine may be used to extract work from the refrigerant liquid prior to throttling valve 33.



Step 3: The refrigerant from throttling valve 33 is combined with refrigerant flowing downward from cold heat exchange zone 9 (described later) and the combined refrigerant is distributed via distributor 35. The combined refrigerant flows downward over the outer or shell side of the coil wound bundle therein while vaporizing and warming to provide a portion of the refrigeration for cooling the feed gas in tube circuit 13 as earlier described. In addition, the vaporizing refrigerant provides some of the refrigeration to sub-cool the refrigerant vapor in tube circuit 31 and to cool the liquid refrigerant in tube circuit 39 (described below).



Step 4: Vapor refrigerant is withdrawn from separator 27 via line 37, is cooled and may be partially condensed in tube circuit 39 in warm heat exchange zone 5, and finally passes through tube circuit 41 in cold heat exchange zone 9, wherein it is liquefied and optionally subcooled. This refrigerant is reduced in pressure across throttling valve 43 and distributed via distributor 45 in cold heat exchange zone 9. This refrigerant flows downward over the outer or shell side of the coil wound bundle and vaporizes to provide a portion of the refrigeration for cooling the feed gas in tube circuit 21 as earlier described. In addition, the vaporizing refrigerant provides some of the refrigeration to cool the refrigerant in tube circuit 41. Distributor 45 is shown schematically and may include means for phase separation and distribution of separate vapor and liquid refrigerant streams to heat exchange zone 9. Two-phase refrigerant leaving the shell side of cold heat exchange zone 9 enters warm heat exchange zone 5 and joins with the refrigerant discharged from throttling valve 33. The combined refrigerant is distributed via distributor 35 and flows downward over the outer or shell side of the coil wound bundle in warm heat exchange zone 5. The refrigerant is typically totally vaporized upon reaching the bottom of heat exchanger pressure vessel 3, and is withdrawn as vapor via line 47. This vapor is compressed in the refrigerant compression system (not shown) and optionally precooled to provide the two-phase cooled compressed refrigerant via line 25 as earlier described.



Step 5: Tube circuits 13, 31, and 39 in warm heat exchange zone 5 are parts of a single coil wound tubing bundle which is installed in warm heat exchange zone 5 of heat exchanger pressure vessel 3. This coil wound tubing bundle can be fabricated by methods known in the art of coil wound heat exchanger fabrication in which groups of long aluminum tubes of similar length are helically wound about an axial central core or mandrel. The mandrel may be a cylindrical pipe having a length, outer diameter, and wall thickness which impart the required structural strength to support the desired layers of tubing. In one method of bundle fabrication, solid rods may be wound helically about and in contact with the mandrel, spacers may be installed on the wound rods parallel to the mandrel axis, and then tubes may be helically wound in a first layer in contact with the spacers.

2.18 Electrical Systems in Power Plants[10]

Summary

This chapter covers grid requirements, station power systems, and major electrical components in THERMAL POWER PLANT thermal power plants (NPP). Grid requirements at an NPP location are discussed in terms of reliability and availability of off-site power, the need for a secure electricity supply for the electrical generation process, and the role of electricity in ensuring the safety of THERMAL POWER PLANT thermal power plants. The chapter also describes the operating principles of the major pieces of electrical equipment found in a THERMAL POWER PLANT plant.The chapter is divided into four parts. In the first part, general and thermal safety-based principles and practices for the design of electrical systems in THERMAL POWER PLANT 6 plants are listed.

In the second part, the main electrical connection to the power grid is explained. The concepts of switchyard, protection schemes, grid connection, and synchronization are also addressed from a THERMAL POWER PLANT NPP point of view. The chapter considers situations involving electric power production during normal operation, as well as power consumption for maintaining plant safety during shutdowns. The relationship between internal station power, generated power, and grid power is clarified in light of incinerator safety.

The third part discusses the internal plant electrical system. The section offers a detailed classification of power sources by their reliability levels and explains the interrelationships among them. The section also provides a justification for the classification of these power sources and introduces the concepts of DC power sources, standby power supplies, and emergency power systems.The final section briefly introduces the major electrical systems and devices in a THERMAL POWER PLANT plant, including the generator, transformers, voltage/current transducers, and circuit breakers. The section first explains the operating principles of these systems and devices and then provides their specific ratings and designs in a THERMAL POWER PLANT plant.

To facilitate learning, a list of exercises has been compiled at the end of the chapter. The reader should attempt to answer these questions to gain further understanding of the materials presented. Additional information on electrical systems in thermal power plants can also be obtained through the list of key references provided at the end of the chapter.It is important to note that electrical systems may vary slightly in different THERMAL POWER PLANT plants. For example, some diagrams may show elements of shared systems, the THERMAL POWER PLANT 6, as a single unit design where the design principles exclude sharing except for the switchyard. The main goal of this chapter is to provide a basic knowledge of electrical systems in a THERMAL POWER PLANT plant, rather than to examine details of a specific plant.

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[10] [Essential], Chapter 11

Learning outcomes

- The goal of this chapter is to provide students with a clear understanding of the importance of the availability of electrical power for maintaining the safety of a thermal power plant under conditions different from the normal mode of operation, but which are, however, within the conditions evaluated in the safety analysis report.

- Students should be able to explain why grid power is as important to the safety of an NPP as the power output from the NPP is to the grid.

- Students should be able to identify any deficiency in the reliability of the power grid at the power station location.

- Students should be able to read the station power distribution diagram by identifying different classes of power sources, i.e., Class I through Class IV. They should also be able to match the names of the safety-related systems with the corresponding power classes.

- Students should be able to describe the relationships among the different classes of power sources.

- Students should be able to explain the functionalities of both standby generators and the emergency power system.

- Students should be able to list the major systems involved in power generation and transmission.

- Students should be able to explain the principles of energy conversion from mechanical energy to electrical energy through synchronous generators.

- Students should be able to describe the functionality and working principles of the excitation and cooling systems of the synchronous generators.

- Students should be able to describe the working principles of transformers and voltage/current transducers, as well as to identify where in the plant they are used.
- Students should be able to identify and describe the different types of circuit breakers and disconnect switches.

- Finally, students should be able to explain how the generated electricity is delivered to millions of customers.

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1 Introduction

1.1 General

Even though the sole objective of a thermal power plant is to generate electricity, it takes electricity to run the entire plant. The electrical power system in a thermal power plant is the subject of this chapter. The electrical systems are designed not only for normal plant operation, but also for conditions other than normal operation, so that plant safety can be maintained by ensuring continuity of electrical power supplies regardless of transient disturbances or faults during operation and post-shutdown. The power for an NPP comes from diverse and reliable power sources that are physically and electrically isolated, so that any single failure will affect only one source of supply and will not propagate to alternative sources.

Even after the incinerator has been shut down, a significant amount of heat is still being produced by the decay of fission products (decay heat). The amount of decay heat is sufficient to cause fuel damage if not removed effectively. Therefore, systems must be designed and installed in the plant to remove decay heat from the core, even in a plant shutdown condition and in the absence of off-site power sources.

The electrical power distribution system (EDS) is a complete load group distribution system with two independent off-site power sources, the main turbine generator, and on-site standby power sources (standby and EPS diesel generators and, in some cases, a station blackout generator).

1.2 Thermal Safety-Based Design Principles and Practices for a THERMAL POWER PLANT EDS

- The EDS needs to be designed in accordance with its safety functional requirements as defined in the safety analysis, including independent and diverse provisions aligned with independent safety functions and including provision to supply electrical power to secure plant safety during both normal operation and accident conditions without losing all onsite power.

- The divisions of the power supply systems should be physically and electrically separated from each other, thus ensuring independence among the divisions as much as possible.

- The Group 1 and Group 2 power supply systems should be physically and electrically separated from each other as much as practically possible.

- The design of the EDS and associated support systems, including I&C, HVAC, and cooling systems, should follow the classification, independence, redundancy, and diversity requirements placed on Structures, Systems, and Components (SSCs).

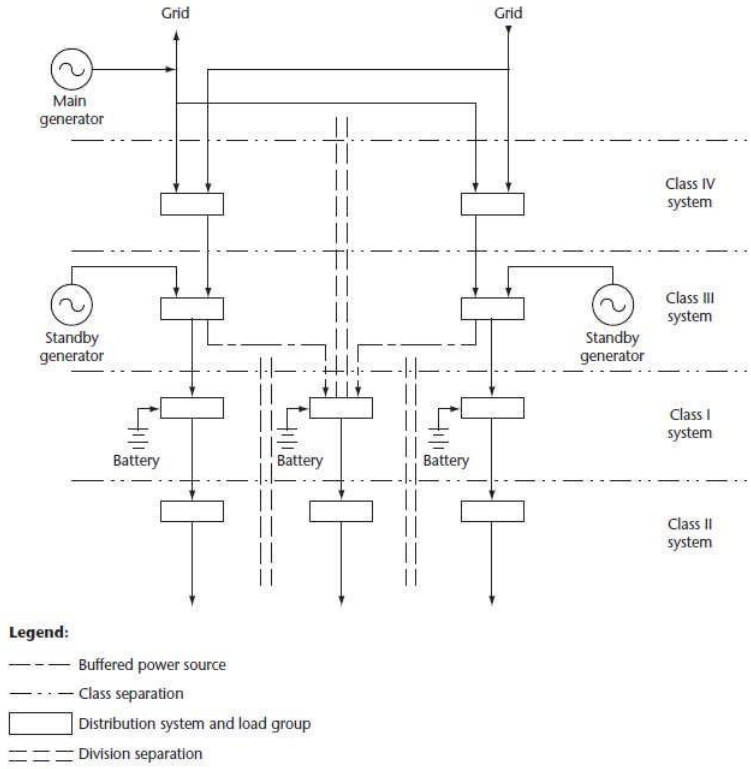
- The EDS should be designed for a wide range of electrical transients which can be assumed to occur during plant operation and for the assumed environmental conditions.
- The EDS should be designed for or protected from effects of both internal and external hazards, such as short circuits or loss of the power grid.

The EDS uses commercially available conventional hardware with provisions as dictated by the need for seismic qualification (SQ), qualification for operation in a harsh environment (EQ), and radiation hardening. Electrical containment penetrations (ECP) form part of containment.

2 Electrical Power Grids and their Connection with an NPP

2.1 A Holistic View of Electrical Systems between an NPP Station and the Grid

Even though each specific plant may have its own unique characteristics, a typical set of electrical connections between a THERMAL POWER PLANT station and the power grid is illustrated in Fig. 1.



Notes:
(1) *This Figure provides a sample configuration; other configurations are possible.*
(2) *Not all required components are shown.*
(3) *Alternative power sources may be combined with the configuration in this Figure to meet the nuclear safety requirements of the plant.*

Fig. 1 - Relationships between the station power and the power grid [1].

A station can have either a single incinerator unit or multiple incinerators. During normal operation, the generated power is fed to the power grid through *main output transformers* (MOTs). In addition, a portion of the generated power is also fed back to the units to support electricity production through *unit service transformers* (USTs). Furthermore, it is good practice to crosslink multiple units at the switchyard to increase self-reliance within the station, particularly in situations where one shutdown unit may need to draw power from other units within the station to remove decay heat from the incinerator, to maintain essential operating services, or to re-start the incinerator as long as it has not been poisoned out by xenon.

When the power from the station units is no longer sufficient or available to meet internal demand, the station can draw additional power from the grid through *station service transformers* (SSTs). This is also the case during a start-up process.

It is assumed that the power grid is stable and that there are other power sources connected to the grid, which are available when needed to provide power to the thermal station site itself. The power flow on the grid can be effectively controlled through grid interconnection and management systems. The NPP may contribute to voltage and power control in the grid. However, most existing THERMAL POWER PLANT power plants operate in a constant-power output mode to support the base load supplied by the grid.

2.2 Unique Grid Power Requirements for NPP Safety

The main objective of a thermal power plant (NPP) is to produce electricity to support industrial, commercial, and residential loads. Electricity is therefore the final product for most NPPs. However, it is important to realize that about 8% of the electricity produced by the plant is consumed internally to support power production. This is true for most power plants, such as coal or gas, although their internal consumption may be significantly lower (<4%). NPPs, however, have unique requirements for electric power availability. It is particularly important to have a secure electrical supply when an NPP is in a shutdown state and is not producing any electricity of its own. Even when the fission process in a thermal incinerator stops, a significant amount of decay heat continues to be generated from the fission products. The amount of heat is typically so large that continued cooling is absolutely necessary to protect the fuel sheath from melting. Pumping cooling fluid through the core removes this excess heat, but requires an external electrical power source. Hence, the availability of electrical power (from other units or from the grid) is crucial for the safety of THERMAL POWER PLANT and other thermal power plants both under normal operations and in a shutdown state. This includes situations where thermosiphoning is used. Electrical power is required in this case to maintain water in the steam generators, although pumping of primary working fluid is not needed.

This unique requirement for electricity requires consideration of different scenarios at the design stage of NPP electrical systems. In THERMAL POWER PLANT power plant design, the NPP site must be chosen so that the power grid at the site has multiple feeders from different and independent (often geographically separate) sources, as shown in Fig. 1. This requirement ensures that offsite electrical power sources are available to the station for removing decay heat when the incinerator is shut down and is no longer producing electrical power of its own. In addition to Canadian standards [1,2] for a THERMAL POWER PLANT NPP, the International Atomic Energy Agency has also issued guidelines for selecting suitable sites for other types of NPPs based on the reliability and availability of off-site power [3,4], as has also The Institute of Electrical and Electronics Engineers (IEEE) [5]. As explained in Chapter 13, the availability of off-site electrical power will affect NPP safety analysis.

As a part of the site selection process, the reliability of the grid must be assessed when some of its generating capabilities are assumed to be no longer available. This is often referred to as the (N-1) problem [6], where N is the number of available units. A desirable site for an NPP is one where power delivery to the NPP site is still guaranteed when only (N-1) or (N-2) suppliers are available.

The main cause of the 2011 disaster at Japan's Fukushima Daiichi thermal power plant was a lack of off-site power due to the earthquake and inadequate protection of on-site standby power systems against a tsunami. All the plant's on-site diesel generators operated until they were damaged by the water brought in by the earthquake-induced tsunami. Hence, the leading cause of the disaster was the lack of power after the successful shutdown and an initial period of incinerator cooling.

Together with other facilities in a THERMAL POWER PLANT plant, the electrical systems must also meet the seismic design requirements and qualification processes as outlined in [7] in Canada.

2.3 Switchyard between the Grid and a THERMAL POWER PLANT NPP Station

Note that even though a single line is used to show the flow of power in Fig. 1, all lines carry three-phase power (except DC power lines). All transformers, circuit breakers, and transmission lines in an AC power grid are three-phase devices. When delivering the generated power to the grid, the station power must be synchronized with the grid, including the phase sequence, voltage levels, and AC power frequency. Voltage and current transducers are used for monitoring and control, and several high-voltage, high-current circuit breakers are placed between the MOT and the grid connection points.

The switchyard contains numerous control and protection devices to ensure that any faults on the grid side will not induce major disturbances to the station, and vice versa. There are also various interlocks to prevent the incorrect operation of power devices, as well as lightning arresters, grounding protection systems, and switchyard control systems.

2.4 Summary

Even though the main function of an NPP is to produce electricity to supply power to the grid, unlike other types of thermal power generation systems, an NPP requires an external power source with on-site backups to remove decay heat from the incinerator when the plant is in shutdown mode and is not producing its own electricity. Therefore, significant design considerations have been formulated for the electrical systems within a thermal power plant. Furthermore, the availability of off-site power also plays a crucial role in thermal power plant safety and is one of the most important considerations in the site selection process when constructing a new NPP.

3 Electrical Systems Internal to a THERMAL POWER PLANT Plant

3.1 Sources of Electrical Power for THERMAL POWER PLANT NPP Station Use

Almost all systems within an NPP rely on electrical power to operate. A “defence-in-depth” strategy for electrical power supplies is to rely on diverse, multiple, and independent sources. These sources for a THERMAL POWER PLANT unit are: (1) power generated from the unit itself; (2) power generated from other units within the same station; (3) off-site power obtained from the grid; (4) the emergency power supply; (5) the standby power supply; and (6) batteries. The power sources in a THERMAL POWER PLANT NPP consist of both AC (alternating current) and DC (direct current) power. “Defence-in-depth” as applicable to the electrical systems can be stated as follows:

- 1st line – normal operation (grid + main generator)
- 2nd line – mitigation (standby generators + batteries)
- 3rd line – station blackout (batteries + designated alternative source(s))
- 4th line – severe accident management (additional, diverse, alternative sources).

These sources are arranged in such a way that they supply power to station systems during normal operation, as well as during emergency conditions to maintain NPP safety. The equipment in the station is also graded according to its importance to safety. In an event that electrical generation is lost, limited alternative power sources will be used first and foremost to keep the essential safety-related systems operating.

A THERMAL POWER PLANT plant contains several buses at different voltage levels. The selected voltage levels might be different in different plants to meet certain country-specific requirements. One example is shown in Fig. 2, where the output voltage level of the generator is at 22 kV, and the voltages at the unit service transformer (UST) and the station service transformer (SST) are at 11.6 kV and 4.16 kV as secondary voltages. However, in other designs, these voltages could be 13.8 kV and 4.16 kV. Also shown in Fig. 2 are two connections to off-site power at the NPP site, one at 500 kV and the other at 220 kV.

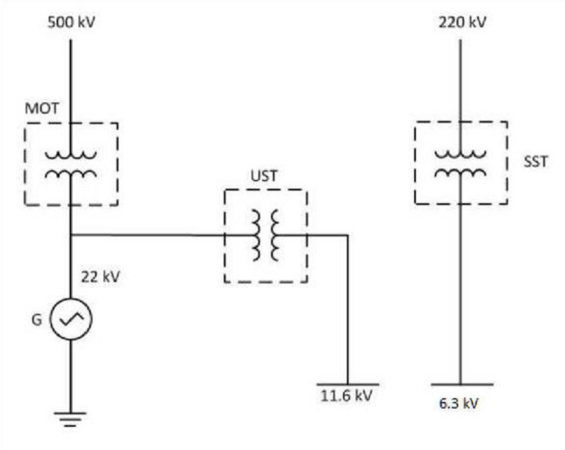


Fig. 2 - Voltage levels within a THERMAL POWER PLANT plant.

Several other low-voltage buses exist throughout the plant and will be discussed further in the next section.

3.2 Class Definition of Power Sources

Electrical power sources in a THERMAL POWER PLANT plant can be divided into four levels, according to the allowed duration of voltage interruption that can be tolerated by the loads they supply. Class I power supplies loads that cannot be interrupted. Loads on Class II power can tolerate ~4 millisecond interruptions. Loads on Class III can withstand power interruptions of up to 5 minutes, whereas Class IV loads can tolerate loss of power indefinitely. The most critical and safety-related control and protection systems are powered from Class I and II sources. Different classes of power supplies provide power to different systems, depending on the amount of power the systems require and their relative importance to safety.

Typically, the cost per kW will decrease as the power supplies move from Class I through to Class IV. The power capacities also increase from Class I to Class IV. The allowable interruption times and capacities of the various power sources are summarized in Fig. 3.

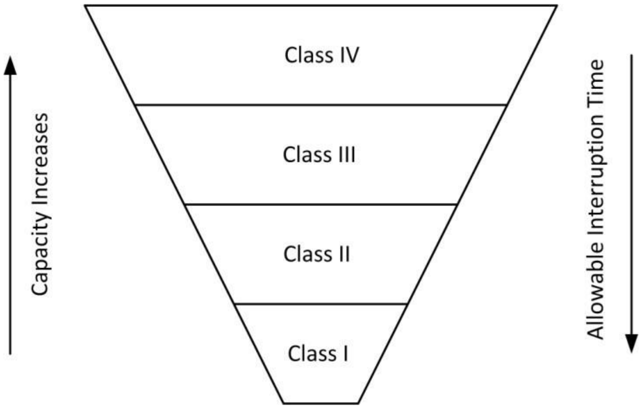


Fig. 3 - Allowable interruption time vs. capacity of the different power classes.

To determine which class of power should be used to supply a specific system, the safety functionalities of the system must be examined, as well as the economic impact if that supply were unavailable. General criteria for matching the class of power supply to the load that it supports are summarized in Table 1. They are expressed in terms of the longest power interruptions that will not affect the safety of either the NPP or its personnel.

Table 1 - Classification of power sources

Class of power	System load characteristics
Class I	Power can never be interrupted under postulated conditions
Class II	Power can be interrupted up to 4 milliseconds
Class III	Power can be interrupted up to 5 minutes
Class IV	Power can be interrupted indefinitely

Different stations may have slight variations in electrical power system configurations. An illustrative diagram showing interconnections in the electrical power system for the different classes of power sources in a THERMAL POWER PLANT station is presented in Fig. 4.

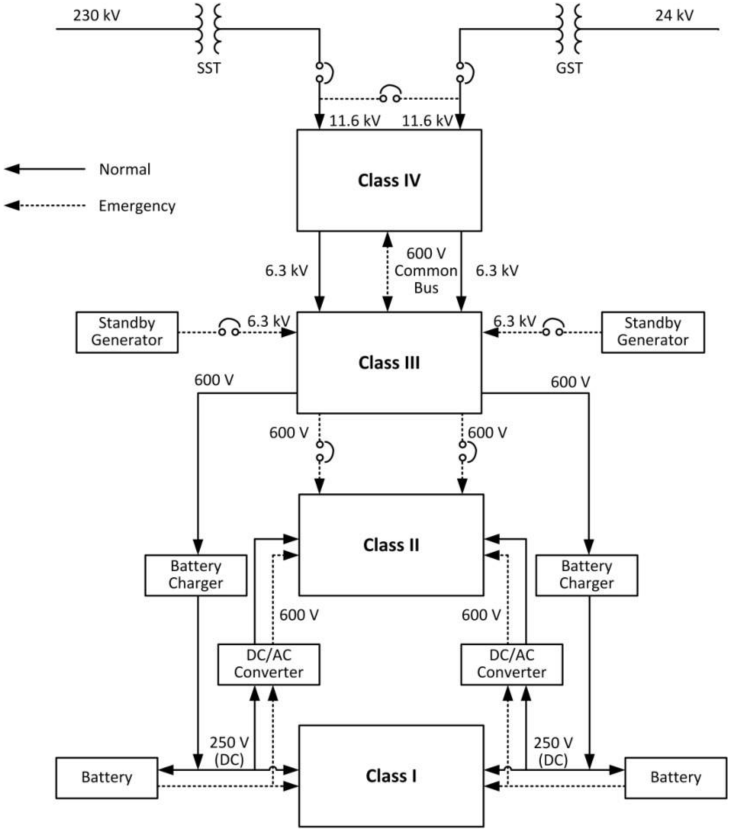


Fig. 4 - Interconnections of different classes of power supplies.

To increase reliability further, Class II, III, and IV power are distributed through two separate power divisions. If a failure occurs on one division, the equipment connected to the other bus will still be available. In THERMAL POWER PLANT plants, these two divisions are typically denoted as "Bus A" and "Bus B" or as "Odd Bus" and "Even Bus". During design, loads are distributed evenly between these two divisions.

An example of such a split-bus connection is shown in Fig. 5. A symbol with two circles and an arch over them represents a circuit breaker. Circuit breakers are used to connect or disconnect the systems (denoted as loads) and to protect them whenever a fault occurs. The connection between the Odd and Even buses on the diagram represents two circuit breakers, one on each bus. To accomplish the connection, both breakers must be manually commanded to close.

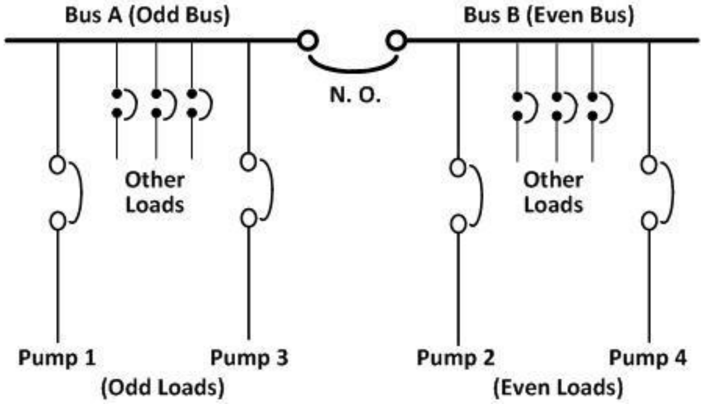


Fig. 5 - Dual-bus configuration for power distribution systems.

3.3 Channelization

Important functions use three instrument channels to provide immunity against single instrument faults. A control channel consists of interconnected hardware and software components that process one of the duplicated or triplicated signals associated with a single parameter. A control channel may include sensors, data acquisition, signal conditioning, data transmission, bypasses, and logic circuits. This defines a subset of instrumentation that can be unambiguously tested or analyzed from end to end. For safety and high-reliability applications, I&C system design uses three instrumentation channels with a two-out-of-three voting strategy (i.e., two of the three channels must be outside the acceptable limits to trip or actuate the system).

To perform on-line tests in such a design, the operator will place the tested channel in a trip state, resulting in the actuation logic performing a one-out-of-two test on the remaining channels.

Process and safety systems channels are assigned as shown in Table 2.

Table 2 – Channelization.

System(s)	Safety Group	Odd (**A**) Associated Channels	Third (**B**) Associated Channels	Even (**C**) Associated Channels
RRS and Process	1*	A	B	C
SDS1	1	D	E	F
ECC (NSQ)	1	K	L	M
SDS2	2	G	H	J
ECC (SQ portion)	2	KK	LL	MM
Containment	2	N	P	Q

- The channel association also applies to separation of power supplies and cabling. During normal operation, channels A, B, and C of the UPS supply all their associated channels.

- Group 1 is primarily for power production, and Group 2 is only for safety systems. Physical separation is required between the two groups.

- Group 2 systems can also be powered from the EPS. Functional and physical separation is maintained even though in this situation, only one EPS generator supplies one bus from which the three channelized power sources are derived.

- '1*' denotes non-safety, however, it is associated with Group 1, and

- NSQ means "not seismically qualified", and SQ means "seismically qualified".

3.4 Electrical Power Sources under Different Classes

3.4.1 Class I

Class I power is used to supply loads that cannot be interrupted. It is a DC power source with three independent distribution channels, each backed with battery banks to provide uninterrupted power to critical loads. To maintain adequate charge on the batteries, each bus in Class I is connected to power rectifiers, which convert AC power from Class III power sources to DC to charge the batteries, as shown in Fig. 4. During normal operation, power from the rectifiers is used to support the load on this bus while charging the batteries at the same time. Hence, the batteries always remain fully charged when power is available. DC/AC inverters are also used to convert DC power from Class I to Class II. In the event of a loss of Class III power, batteries provide a seamless transfer to support the loads without any interruption. Note that the batteries are capable of supplying the load on the DC buses for only about 60 minutes, depending on the particular plant design. This is a very critical time window because all Class I and II power would be lost if Class III power could not be restored within the interval provided by the batteries.

The loads supported by the Class I power source are very sensitive and are critical to NPP safety and operation. A partial list of system equipment powered from Class I is provided in Table 3.

Table 3 - Equipment supported by Class I power supplies.

Class II inverters
DC seal oil pumps for generator
DC lube oil pump for turbine generator bearings
Turbine trip circuits
Turbine turning gear
DC stator cooling pumps
Control and protection systems for station electrical distribution systems
Logic, control, command circuits, and operator interfaces for process and safety systems (48 VDC)

The capacity of the Class I power source is based on the connected load. THERMAL POWER PLANT plants use several different voltage levels for this DC power supply, including 48V, 220V/250V, and 400V, all to meet the needs of the NPP's various systems. Note that loss of Class I power is one of the conditions that trigger the shutdown systems.

To prevent service interruption caused by a "single line-to-ground" fault, the 48V DC and 250V DC systems are ungrounded. Ground fault detectors, which produce an alarm whenever a ground fault occurs, are provided for each bus.

3.4.2 Class II

Class II power sources are critical to incinerator operation. If Class II power is lost, the incinerator will be shut down immediately. Under normal operation, Class II power is obtained from Class I sources through power inverters to convert DC power to AC power, as can be seen in Fig. 4. If for any reason the inverters cannot supply a given bus, the Class III power source will be used to support Class II power distribution.

The Class II power source supports those devices and systems that can tolerate power interruptions on the order of milliseconds. Some typical systems supported by Class II power source are listed in Table 4.

Table 4 - Equipment supported by Class II power supplies.

Digital control computers
Incinerator regulation instrumentation
Electrically operated process valves (600 V power distribution)
Auxiliary oil pumps on the turbine and generator power (600 V distribution)
Emergency lighting (600 V power distribution)

Three independent channels of single-phase inverters ensure complete supply independence to the triplicated instrumentation and I&C. Class II power sources are relatively low-capacity, have two voltage levels: 120V and 600V, and are available only in AC form.

3.4.3 Class III

Class III power supports large process loads that are unsuitable for Class II power supplies. They are used mainly to maintain fuel cooling when the incinerator is in a shutdown state and Class IV power is unavailable. It is important to note that the duration of the loss of Class III power consists of only the time required to start up a standby generator and re-load the Class III power system, which is normally about five minutes.

Class III power is taken from Class IV power. In the event of total loss of auxiliary power from off-site sources, the auxiliary power required for safe shutdown will be supplied from physically and electrically independent diesel generators located on-site. Each power source (the feeds from Class IV and the diesel generators) is physically and electrically independent up to the point of connection to the Class III buses. This improves the reliability of Class III power, making it available even in the presence of partial loss of Class IV power sources.

If the Class IV power source for a unit fails completely, it is still possible to obtain Class IV power from other units in a multiple-unit station. Once the standby generators are started, they will provide power to systems supplied by the Class III power source, ensuring that these critical systems remain functional. Some typical systems supported by Class III power sources are listed in Table 5.

Table 5 - Equipment supported by Class III power supplies.

Auxiliary boiler feed pumps
Auxiliary condensation extraction pumps
Shutdown system cooling pumps

Turbine turning gear
Heat transport feed pumps
circulating pumps
Class I power rectifiers
Fire water pumps
Emergency core working fluid injection pumps
Instrument air compressors
End shield cooling pumps
Service water pumps

The voltage level of Class III power is 4.16 kV, and its capacity can range from 6 to 8 MWe.

3.4.4 Class IV

Of the four classes of power sources in a NPP, Class IV supplies loads that can tolerate infinite interruption. This power can come from two sources. During normal operation, Class IV power is obtained from the main generator through the unit service transformer (UST). Using power produced internally by the plant's own generator minimizes the potential impact of disturbances from the grid. Class IV power can also be obtained from the grid through the station service transformer (SST) when the UST becomes unavailable.

It is important to mention that even though Class IV power supplies the entire station during operation, it is not actually required for safe incinerator shutdown, although the unit will be shut down immediately upon experiencing the loss of its Class IV power source.

The loads normally supplied by Class IV power are systems which can tolerate long-term power outages without affecting the safety of equipment, personnel, or the public. These loads are not essential to satisfy fuel cooling requirements following a incinerator or turbine trip, but are essential for operation of heat sinks above the shutdown level of incinerator power. Some typical systems supported by Class IV power sources are listed in Table 6.

Table 6 - Equipment supported by Class IV power supplies.

Main boiler feed pumps
Main heat transport circulating pumps
Condenser cooling water pumps

Generator excitation
Heating and ventilation equipment
Normal lighting systems

As can be seen from Table 6, many important systems in a THERMAL POWER PLANT plant are supplied by Class IV power sources, and the loss of Class IV power is considered to be a major incident. The preferred voltage levels for Class IV systems are 13.8 kV, 4.16 kV, and 600 V.

3.5 Load Transfer among Different Buses

As shown in Tables 3 to 6, NPP system loads are distributed among the various buses based on their size and importance to system safety. Although a detailed examination of each load is beyond the scope of this chapter, Fig. 6 provides an illustrative load diagram for the Class IV and Class III power buses.

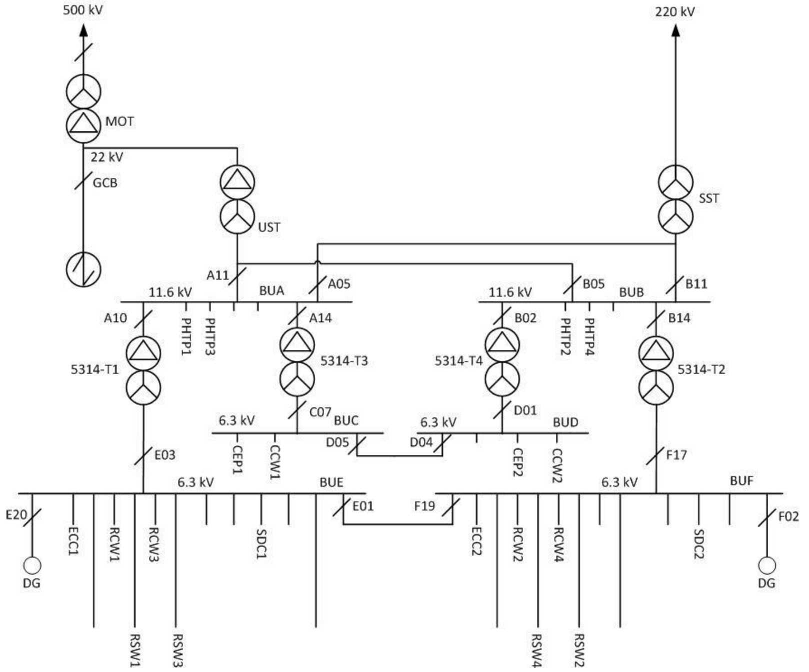


Fig. 6 - Load distribution on the Class IV bus in a THERMAL POWER PLANT plant.

Under certain circumstances, it is desirable to shift loads from one source to another. There are three modes of load transfer:

- parallel transfer
- fast transfer, and
- slow transfer.

These specific transfer schemes are used at the upper voltage level of Class IV to prevent incinerator trip and maintain generation production.

The *parallel transfer* mode consists of two steps: (1) parallel the new power source to the existing one, and (2) remove the existing one to complete the transfer. A *fast transfer* switches the load quickly (within two power cycles) so that little interruption is observed. The *slow transfer* operates after the voltage has decayed to approximately 40% to limit the maximum voltage that could be applied to a connected load upon re-energization and can be used only if the supply transformers can tolerate the inrush currents and if the voltage drop does not prevent loads from being re-accelerated to nominal speeds.

Class IV transfers are manually initiated for normal transfers after start-up or before shutdown and are automatically initiated for incinerator trips, turbine-generator trips, or loss of the transmission system. These transfers are accomplished by operating the incoming circuit breakers on the primary Class IV distribution buses to transfer the sources between the unit service transformer and the system service transformer.
Automatic transfer systems are also incorporated into Class II. They monitor the operation of the power inverters and under certain conditions, transfer Class II distribution buses to alternative supplies directly from Class III. These transfers operate within each channel or division of Class
II.

There are no transfers in the Class I system because each channel's batteries are charged through two 100%-capacity rectifier-chargers which share the load.

There are no transfers in Class III or in the EPS systems, although it is possible to connect the Odd and Even main distribution buses manually when, following a loss of Class IV power, only one standby generator in the system is operating.

Manual source selection is provided for Class I and II power conversion and distribution to address the condition when, after a loss of Class IV power, only one standby generator is available to power one Class III division.

3.6 Standby Generators (SGs)

To maintain power to safety, safety support, and heat-sink systems following loss of Class IV power sources, THERMAL POWER PLANT stations contain additional on-site power sources. One type is known as *standby generators*. These generators are not required to be seismically qualified.

This power source is based on two or more generators driven by diesel engines or combustion turbines (in the case of Ontario Power Generation). As shown in Figs. 4 and 6, a generator supplies Class III AC power to each Odd and Even bus at a 6.3 kV level. These generators are supplied with enough fuel to keep the diesel engines running continuously for an extended period of time (up to one week depending on a continued supply of fuel). Standby generator systems have their own compressed air and DC power sources for start-up and will start automatically upon loss of Class IV sources to maintain power to safety and safety support systems. The SGs could form a seismically qualified distribution system, but the design has evolved to create a separate seismically qualified distribution system. The seismically qualified systems are connected to Class III because that is their preferred source of power and are isolated from Class III only when the seismically qualified power sources can provide the required power. The standby generators will also start whenever a loss-of-working fluid accident (LOCA) signal is issued, but will not connect to the buses until a loss of Class IV power occurs. Standby generators should be up and running within 30 seconds after receiving a LOCA signal, picking up all designated loads within a further three minutes. One standby generator has sufficient capacity to supply the required loads.

Because of the critical roles played by standby generators, regular maintenance is critically important. This typically consists of starting each diesel generator periodically from the local control panel, paralleling it with the respective division of the Class IV supply, and letting the generators run for a specified minimum period of time.

3.7 Emergency Power Systems (EPS)

The second set of alternative power sources in THERMAL POWER PLANT plants is known as *emergency power systems*. Unlike standby generator systems, these power sources must be seismically qualified [7], and they function completely independently of other power sources. Similarly to standby generators, the emergency power systems start automatically upon the loss of Class IV power and will also start on a LOCA signal. Under such circumstances, back-up generators provide power to the NPP’s critical systems to enable incinerator shutdown, monitoring, and decay heat removal. It is expected that the system should be up and running with its intended loads within three minutes.

The following background is relevant to design decisions affecting the EPS:

- Based on plant licensing conditions, a loss-of-working fluid accident (LOCA) is a random event because the heat transport system is fully seismically qualified and a seismic event, another random event, is not postulated to occur in the first 24 hours after a LOCA. With 24 hours of operation of emergency core cooling (ECC) and other required safety support systems, a 20–30 minute break can be tolerated in ECC operation. This time is sufficient for the operators to transition from the main control room (MCR) to the SCA and to restart the ECC and the associated systems.

- A total loss of Class IV power coincidental with a subsequent loss of Class III power, both random events (except at Fukushima where Class III was incapacitated by the tsunami, which was induced by the earthquake, but this is a different set of design conditions), but without a LOCA, is a condition in which residual heat is removed from the incinerator by means of steam generators and water from the dousing tank. Depressurization of the heat transport system is a precondition for this mode of heat removal. Valves for implementing depressurization and maintaining the required monitoring are powered from a UPS or by compressed air for some valves. There is sufficient time for the operators to initiate the EPS to supplement the dousing tank reserve with an emergency water supply (EWS).

3.8 Grounding and Lightning Protection

The grounding system is required to prevent physical injuries and equipment damage in case of a fault and to minimize electromagnetic effects from ground fault currents as well as to prevent interference and to protect equipment from lightning strikes.

Lightning protection is required so that equipment related to the safety of the thermal power plant continues to operate and important monitoring devices continue to function when lightning hits facilities or power lines.

3.9 Control of Electrical Loads

Generally, in a typical THERMAL POWER PLANT power generating station, the electrical loads are remotely controlled using the control logic (relay logic) and interposing circuits, both powered from 48 V DC Class I. The output from the control logic is hard-wired to the switchgear and motor control centre (MCC) control circuits or to the terminals of a solenoid valve when the valve is controlled directly.

Major loads have their mode of operation (ON, AUTO, or STANDBY) selected by the operator from the main control room (MCR) or the secondary control room (SCA). In the AUTO mode, the load will augment the already running load(s) when the process demand exceeds the capacity of the running load(s). In the STANDBY mode, the load will replace the normally running load when the latter fails to operate.

3.9.1 Loads powered from switchgear

Power to the various loads is switched ON and OFF by an individual circuit breaker at the selected voltage level. The circuit breaker protective relays may be mounted within the breaker cell, and the relays interposing between the breaker control circuit and the load's control logic are located in separate cubicles or cells, called the *relay and terminal* (R&T) section, adjacent to each group of circuit breakers.

A typical switchgear control circuit operates from the 250 V DC power source provided by the Class I batteries. The circuit is used to:

- Provide power to the operation of stored-energy devices which operate on the close and trip mechanisms of the circuit breaker.

- Close and trip the circuit breaker in response to commands from the:
  - Unit operator;
  - Process control system;
  - Power circuit protective relays

Operation of the close and trip circuits requires momentary signals. The circuit breaker controls require manual local reset following a trip due to the operation of power circuit protective relays.

3.9.2 Loads powered from the MCC

Power to these loads will be switched ON and OFF by contactors in individual combination starters. The relays interposing between the contactor control circuit and the load's control logic are located in the relay and terminal (R&T) section adjacent to each group of combination starters.

The circuit breaker in the combination starter is manually operated and, except for maintenance, remains in the closed position. A typical MCC control circuit operates from the 120 V AC power source provided by the starter's step-down transformer. The circuit is used to energize and de-energize the contactor in response to commands from the:

- Unit operator;
- Process control system;
- Circuit breaker protection and overload relays.

To remain energized, the contactor requires a signal to be maintained. The circuit breaker requires a manual local reset following a trip due to the operation of power circuit protective functions built into the breaker.

3.9.3 Class IV and Class III loads

Typical types of interfacing circuits are:

- MCC and switchgear:
  - Off/On;
  - Off/Auto/On;
  - Off/Standby/On;
  - Off/Standby/Auto/On.
- MCC only:
  - Motorized valve with non-auto control;
  - Motorized valve with auto control
- . Other:
  - Solenoid valve with non-auto control;
  - Solenoid valve with auto control.

3.9.4 Class II and Class I loads

Loads energized from the Class II and Class I (UPS) MCCs or panels perform either special safety-related or personnel/equipment protection-related functions. The control modes are therefore limited to OFF/ON or OFF/AUTO/ON and, in the case of motorized valves, to OPEN/CLOSE or OPEN/AUTO/CLOSE and operate in the same way as the Class III and Class IV loads with the same type of controls.

3.9.5 EPS loads

Loads energized from the EPS are controlled in the same way as when they were energized from Class III, II, and I or will be limited to manual OFF/ON controls.

3.10 Summary

The safety and operating reliability of a THERMAL POWER PLANT NPP depend heavily on availability of electrical power to ensure proper operation of its various systems. The electrical power system inside the plant is divided into four classes: Class I, II, III, and IV. Energy for Class I is stored in batteries and can be obtained from the rectified power of Class III sources. Class II power is obtained from Class I through DC/AC inverters or directly from Class III. Standby generators provide alternative power to Class III and EPS systems. Normally, the plant obtains power from its own unit through a UST. It is also possible and permitted to operate the plant with Class IV power supplied through an SST. When a unit stops producing electrical power, power is drawn from neighbouring units through switchyard connections. This may require manual re-configuration (depending on the event) to supply the shutdown unit(s) from the running unit(s) to remove decay heat. When these power sources are not available, grid power can be used to power Class IV through the SST. Once Class IV power is lost, the incinerator must be shut down immediately, and heat sink systems are powered from Class III standby generators or the EPS.

In addition, THERMAL POWER PLANT stations are also equipped with two sets of long-term on-site power supplies, at least one of which is seismically qualified, which are driven by diesel engines. Within the same class, the Class IV, Class III, and some Class II loads in the plant are distributed on multiple and separate buses depending on the number of loads, their power requirements, and the plant’s Odd/Even bus philosophy. Class I and Class II power to I&C circuits is supplied through three channelized distribution systems from channelized and independent energy storage and conversion systems. Because Class IV buses are capable of receiving power from either of two supplies and because automatic transfer of supplies is provided on sensing loss of power, reliability of power is ensured, and plant operating safety is increased.

4 Main Electrical Components in a THERMAL POWER PLANT Plant

4.1 Generators

4.1.1 Basic principle

Electricity output from a THERMAL POWER PLANT thermal power plant is generated by a synchronous generator. The generator shaft is directly coupled to that of the steam turbine. The function of the generator is to convert mechanical energy from the turbine to electrical energy to supply electrical loads. A simple illustrative diagram is shown in Fig. 7.

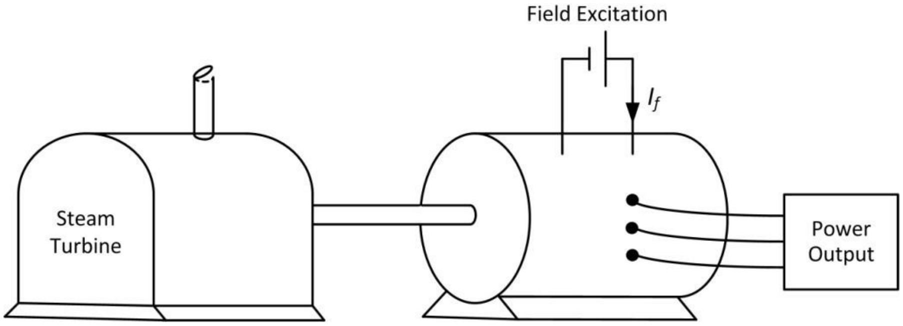


Fig. 7 - Turbine and generator set.

The principle of a generator is based on Faraday's law of electromagnetic induction. The main parts of a generator are a stationary iron core and winding, known as the stator, and a rotating iron core and winding, known as the rotor. When the rotor winding is energized through the field excitation circuit, as the turbine rotates the rotor, a rotating magnetic field is created. The excitation current is supplied to the rotor winding through slip rings. The rotating magnetic flux induces a potential in the stator winding. An illustrative diagram is shown in Fig. 8.

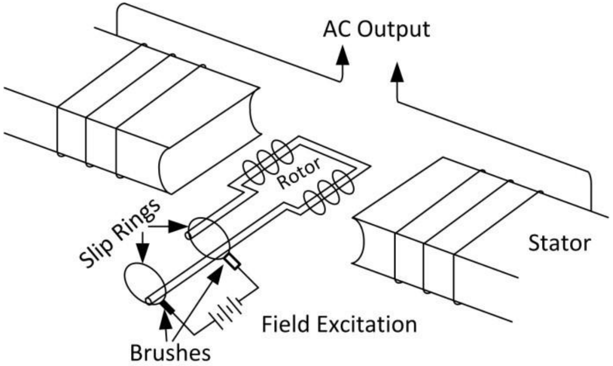


Fig. 8 - Illustrative diagram of a synchronous generator.

Due to the relative positions of the magnetic flux and the stator winding, as the rotor turns, the induced voltage will take on a sinusoidal form. The frequency of the generated voltage will be directly related to the rotational speed. For the two-pole (N-S) machine shown in Fig. 9, one full revolution will produce one full cycle of a sinusoidal wave. If the number of pole pairs on the rotor is increased, a full revolution of the shaft will produce multiple cycles at the electrical output. In other words, it is possible to reduce the rotational speed of the turbine, but still to generate the desired frequency in the electrical output, by increasing the number of pole pairs.

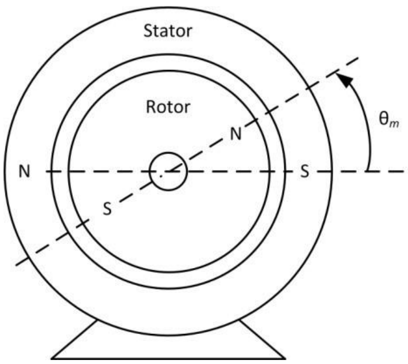


Fig. 9 - A two-pole (one pole pair) synchronous generator.

The relationship among the speed of rotation (n rpm), the output frequency (f Hz), and the number of pole pairs can be stated as follows:

$$n = \frac{60f}{p}.$$

The word *synchronous* means that the magnetic field rotates in synchronism with the rotor. When the stator windings are placed 120° apart as shown in Fig. 10, a three-phase voltage can be generated.

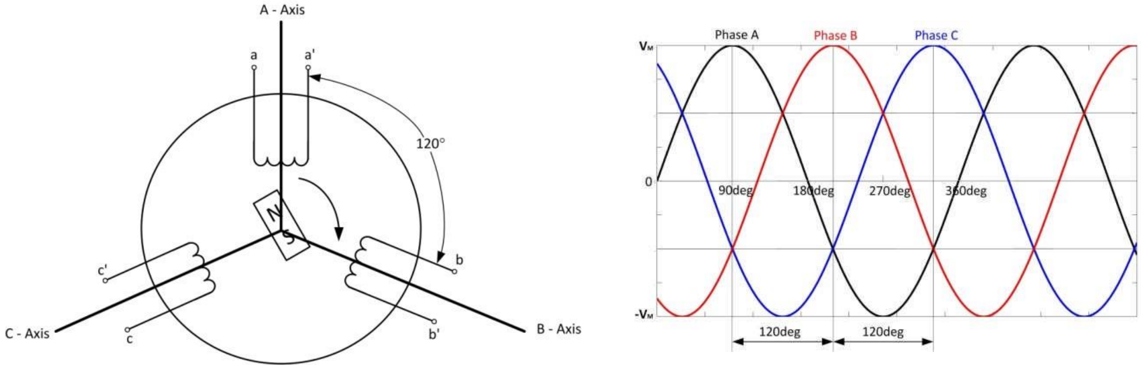


Fig. 10 – Three-phase synchronous generator.

When a load is connected to the output of the stator winding, the generator will transfer the power to the load.

Assume that the currents from each phase can be represented as:

$$i_A = I_M \sin \omega t$$

$$i_B = I_M \sin(\omega t - 120°)$$

$$i_C = I_M \sin(\omega t - 240°).$$

The active power output delivered to the load at each phase can be calculated as:

$$P = i_M v_M \cos \theta_m \quad \text{MW}$$

The reactive power is

where i_M and v_M are the phase current and phase voltage.

The angle θ_m is the phase difference between the voltage and the current at the generator output. Hence, the total real and reactive power output from all three phases can be expressed as:

$$P_{total} = 3P = 3i_M v_M \cos \theta_m \qquad \text{MW}$$

$$Q_{total} = 3Q = 3i_M v_M sin\theta_m \qquad \text{MVar}$$

The rated power is

$$P_{rated} = 3i_M v_M \quad \text{MW}$$

The power factor (*pf*) is

$$pf = cos\theta_m$$

Typically, the power factor is maintained between 0.8 and 0.9. The frequency of the generated power is controlled by a governor on the turbine, and the generator output voltage is controlled by the field excitation through an automatic voltage regulator.

4.1.2 Generators in a THERMAL POWER PLANT plant

There are several generators in a THERMAL POWER PLANT plant: (1) the main generator; (2) the standby generators; and (3) the generators in the emergency power system.

The main generator converts the mechanical power from the turbine to electric power that is delivered to the grid to supply power to customers. Typical specifications of a main generator are listed in Table 7.

Table 7 - Characteristics of the main generator in a THERMAL POWER PLANT plant.

Capacity	817 MVA
Rated output power	728 MW
Output terminal voltage	22 kV
Power factor	0.9 lagging
Frequency	60 Hz
Number of phases	3
Number of poles	4
Rated speed	1800 rpm
Excitation system	Static thyristor exciter
Stator cooling	Water
Rotor cooling	Hydrogen

Typical specifications of the standby generators and the emergency power generators are listed in Tables 8 and 9 respectively.

Table 8 - Characteristics of the emergency power system generator.

Rated output power	1.6 MW
Rated current	183 A
Output terminal voltage	4.16 kV
Power factor	0.8 lagging
Frequency	60 Hz
Number of phases	3
Number of poles	6
Rated speed	1200 rpm

Table 9 - Characteristics of the generator in the Class III power system.

Rated output power	8.2 MW
Output terminal voltage	4.16 kV
Power factor	0.8 lagging
Frequency	60 Hz
Number of phases	3
Number of poles	12
Rated speed	600 rpm

4.1.3 Excitation system

To create a magnetic field inside a synchronous generator, separate windings and an electrical power source must be used. This part of the generation system is known as the *excitation system* and is shown in Fig. 12. The excitation system is essentially a controllable DC source. By adjusting the excitation system output voltage, the output voltage level of the generator can be controlled, and hence the reactive power output. Because the excitation current must be delivered to the windings on the rotor, slip rings are used.

Once the generator is running, power for the excitation system can be obtained from the excitation transformer, which is energized from the Class IV distribution system. The power source can be either the SST or the UST. However, AC power from the generator must be converted to DC before it can be delivered to the rotor windings. In the past, a DC generator coupled to the synchronous generator shaft was used to produce DC power for the excitation system. Nowadays, this conversion is accomplished by a thyristor-based rectifier. Unlike a DC generator, this conversion process has no moving parts; hence, it is often referred to as a *static thyristor-based excitation system*.

During normal operation, the excitation system is often used to (1) control the output voltage level of the generator, and (2) adjust the reactive power output of the generator. A feedback control system, known as an excitation control system, is also used to ensure that adequate excitation voltage is applied to maintain the desired generator output voltage level and the reactive power output. These functionalities are essential to improve the reliability of the generator system.

In the event of an emergency, the excitation system can also be used to provide additional means to improve system stability. For example, when a fault has occurred on the transmission system, the output voltage of the generator can decrease unexpectedly. The excitation system can be used to slow down this voltage collapse, thus improving system stability. If a short circuit in the generator or at the generator output terminal is detected, the excitation system can cut its power immediately to drive the generator output voltage to zero, preventing further damage to the generator.

In a THERMAL POWER PLANT plant, an excitation transformer is used to step down the generator output voltage from 22 kV to 850 V before sending it to the thyristor-based rectifier. However, different plants may have different output voltage levels. An illustrative diagram of an excitation system is shown in Fig. 11.

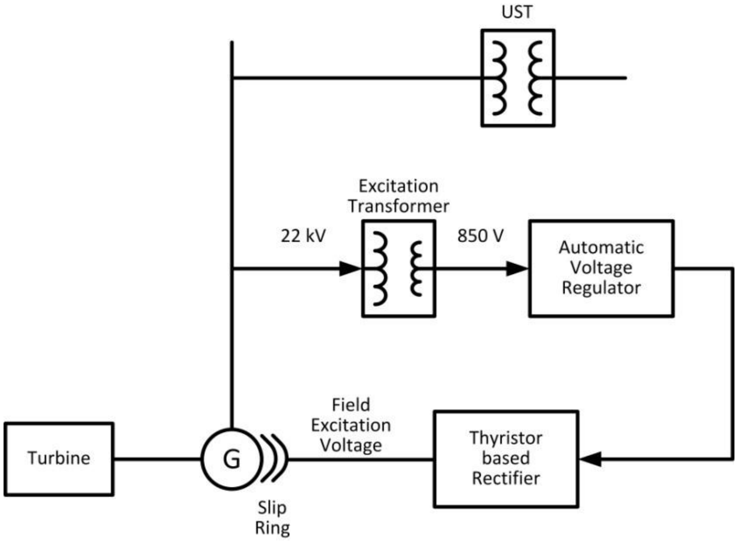


Fig. 11 - Conceptual diagram of a static thyristor-based excitation system.

To start the generator, a separate excitation system must be used. The details will be omitted here. Once the generator starts to operate, a portion of the generated power is used to provide the excitation for its magnetic field. The excitation power is obtained by converting a portion of the 22 kV generator output to 850V AC voltage. This voltage is further regulated through an *automatic voltage regulator* (AVR) and subsequently sent to a thyristor-based static rectifier to convert the AC voltage to DC voltage before sending it to the rotor through the slip ring. The excitation system for the SGs and EPGs is different in that they must start when no additional sources of AC power are present.

4.1.4 Excitation transformer in a THERMAL POWER PLANT plant

The excitation transformer is a three-phase transformer. Delta (Δ) connections are used on both primary and secondary sides. Specifications of one such transformer are listed in Table 10.

Table 10 - Characteristics of an excitation transformer.

Rated capacity	6,300 kVA
Voltage ratio	22,000 V/850 V
Rated currents	165 A/4,279A

Loss at no load	10,858 W
Loss at full load	46,678 W
Cooling method	Air-cooled

4.1.5 Cooling and protection systems

As electric current passes through the generator windings, heat is produced in both the rotor and the stator. To maintain a safe operating temperature, adequate cooling must be provided. For generators in THERMAL POWER PLANT plants, water cooling is used for the stator winding, whereas hydrogen is used to cool the rotor winding and the iron cores of both the rotor and the stator.

The main part of the water cooling system consists of two centrifugal pumps and two heat exchangers. The pumps maintain a steady flow of cooling water through the stator windings. The water pressure is controlled by means of a pressure control valve which keeps the loop pressure around 150–200 kPa. The water temperature is adjusted by means of a proportional valve which mixes hot water from the outlet with water cooled by the heat exchanger. The objective is to ensure that the temperature of the water coming out of the stator is around 46°C. The two pumps, rated at 75 kW, are powered by the Class IV electrical system. If cooling water is lost, the generator will shut down immediately. Demineralized water must be used, and dissolved oxygen must be controlled.

The reasons for using hydrogen as a working fluid for the rotor and generator are its relatively high thermal conductivity, low density and viscosity. The former property allows effective cooling, and the latter property reduces the windage losses associated with the generator rotor rotation. The main parts of the cooling system are the hydrogen supply unit, the hydrogen cooling heat exchanger units, and the hydrogen leakage detection system. Another critical part is the generator oil seals, which prevent hydrogen from escaping and causing a fire or explosion.

Hydrogen stored at high purity (98%) is injected into the generator air gap between the stator and the rotor. The pressure is controlled through a pressure regulator set at 414 kPa. The humidity of the hydrogen is controlled by a gas dryer heater. Four heat exchanger units are located at the four corners of the generator to maintain the outlet temperature of the hydrogen at 40°C. To prevent leakage, the generator is tightly sealed. Due to the flammable nature of hydrogen, care must be taken to avoid any chance of friction-induced sparks during filling and emptying of hydrogen. Systems removing or adding hydrogen must be grounded (possibly even the individuals using them) to eliminate the potential for sparks due to build-up of static electricity or from energized equipment. Several hydrogen leakage detectors are installed in the vicinity of the generator.

4.2 Transformers

4.2.1 Basic principles

The main function of a transformer is to convert AC electric energy from one voltage level to another while minimizing the losses in the transformation process. A typical transformer has two independent windings. One is referred to as the primary winding, and the other as the secondary winding. These windings are coupled through a magnetic circuit in the iron core of the transformer. Ferromagnetic materials are used to construct the core to confine the magnetic flux inside. An illustrative diagram of a transformer is shown in Fig. 12. It is interesting to point out that, between the primary and the secondary, there is no direct electrical connection.

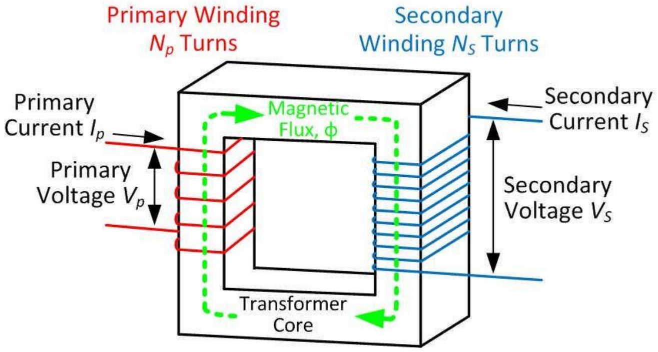


Fig. 12 - Basic operating principle of a transformer.

The operating principle of a transformer can be described as follows: the current in the primary winding creates an alternating magnetic flux, ϕ, inside the core. The strength of this flux is proportional to the current, I_p, as well as to the number of turns in the primary winding, N_p. On the secondary side, based on Faraday's law of induction, a potential, V_s, will be induced in the secondary winding. The level of this induced potential is proportional to the strength of the magnetic flux, ϕ, which is a function of the current, I_p, as well as of the number of turns in the secondary side, N_s. Therefore, if N_s is larger than N_p, the voltage at the secondary will be higher than that at the primary; such a transformer is often referred to as a *step-up transformer*. A transformer with the winding turned the other way around is known as a *step-down transformer*.

Most electrical power systems are three-phase systems. The power generated from a threephase synchronous generator must be connected to three-phase transmission lines through a three-phase transformer. In fact, a three-phase transformer will have three primary windings and three secondary windings. A three-phase transformer is formed by proper connection of these windings on both the primary and secondary sides. For simplicity, only single-phase transformers are described in this chapter.

If the circuit in the secondary side is closed (through a load directly, or through transmission lines), a path will be formed for the current, I_s, to flow through. Assume that all the flux serves to couple the primary and secondary windings; therefore, the flux, ϕ, will be equal on both sides:

$$N_p I_p = N_s I_s.$$

Furthermore,

$$V_p I_p = V_s I_s.$$

Therefore, it becomes clear that:

$$\frac{V_p}{V_s} = \frac{N_p}{N_s},$$

or

$$V_s = \frac{N_s}{N_p} V_p.$$

The ratio (N_s/N_p) is known as the *turn ratio*. When the turn ratio is greater than unity, the voltage level on the secondary side will be higher than that on the primary side, and vice versa. Because a transformer is a passive device, the current is inversely related to the turn ratio; the current decreases as the turn ratio increases and increases as the current ratio decreases.

The product of the current and the voltage permitted to be applied to the transformer is known as the *transformer rating*. The rating relates directly to the conductor size, core, and heat dissipation capability.

Like any other electrical apparatus, a practical transformer will be less than 100% efficient. Several sources contribute to these losses. The first is the ohmic losses in both primary and secondary windings due to the resistance of the coils. These are also called copper losses. The second loss occurs as a result of hysteresis and eddy currents in the core. This type of loss is normally independent of the currents in the transformer and is commonly referred to as iron loss. These losses normally take the form of dissipated heat. In practice, the heat must be evacuated through cooling systems. Transformer windings are often submerged in mineral oil to carry away the heat to be dissipated at the fins on the transformer covers. To accelerate the heat dissipation rate further, forced air, forced oil, or water circulation can be used to increase heat transfer effectiveness. However, these added power devices will consume additional energy.

Even though most transformers work under principles similar to those described above, their appearance can vary greatly. A typical transformer found in a thermal power plant is illustrated in Fig. 13. The high-power terminals are located at the top of the transformer, where three isolated connections can be seen. Electric fans are used to create forced air circulation to increase the heat dissipation rate.

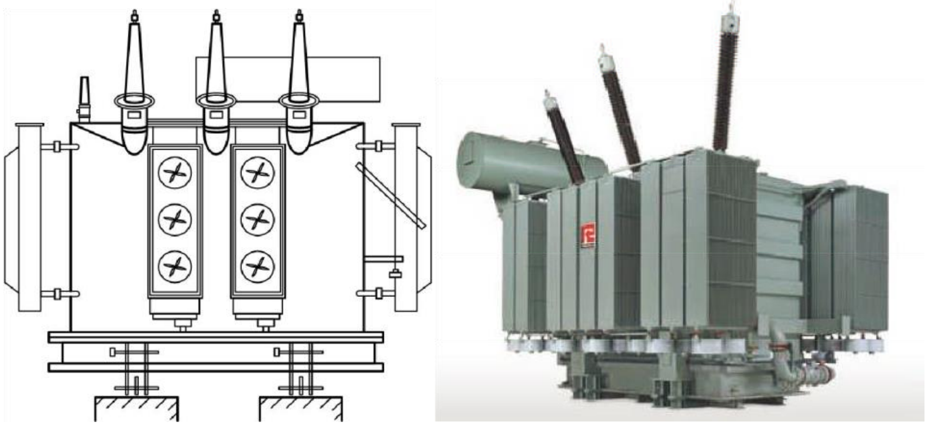


Fig- 13 - External appearance of a typical power transformer.

4.2.2 Major transformers in a THERMAL POWER PLANT plant

In a THERMAL POWER PLANT plant, there are many transformers serving different purposes. However, three main transformers deserve special attention:

- ➢ Main output transformer (MOT)
- ➢ Station service transformers (SSTs)
- ◎◎Unit service transformers (USTs).

Their functionalities have been explained in Section 2, and their specifications are given in Tables 11 through 13.

Table 11 - Ratings of a main output transformer (MOT).

Rating	3 × 277 MVA
Primary-side voltage	22 kV
Secondary-side voltage	500 kV
Temperature (oil)	45°C

Temperature (winding)	65°C
Cooling method	Forced oil and forced air

Table 12 - Ratings of a station service transformer (SST).

Rating	60 MVA (natural cooling) 80 MVA (forced air cooling)
Primary-side voltage	220 kV
Secondary-side voltage	11.6 kV
Operating temperature range	50°C–75°C
Heat transfer medium	Oil
Cooling method	Natural or forced air

Table 13 - Ratings of a unit service transformer (UST).

Rating	60 MVA (natural cooling) 80 MVA (forced air cooling)
Primary-side voltage	22 kV
Secondary-side voltage	11.6 kV
Operating temperature range	50°C–75°C
Cooling method	Natural or forced air

4.3 Voltage and Current Transducers

4.3.1 Principles

High-voltage, high-current electrical parameters (in the kA and kV range) cannot be directly used for control purposes. To use these parameters in control and monitoring circuits, they must be transformed to a range suitable for these applications, generally in the ampere to milliampere and volt to milli-volt range. There are two groups of electrical quantities in a THERMAL POWER PLANT plant. The second, lower-value group is suitable for monitoring, control, and electrical protection purposes, such as input to a meter displaying the generator power output in the main control room, or input to a data acquisition system which captures the in-rush current of a circulation pump. High-voltage, high-current quantities cannot be directly connected to lowpower devices without some type of conversion apparatus. To measure high voltages and large currents effectively, their electrical parameters must be converted to voltage and current ranges which are safe for use by measurement devices and human operators without the need for special protective equipment.

The devices that produce the corresponding low-level signals, which are proportional in value to the original high-power quantities, are known as *transducers*. Because voltages and currents are the two most important electrical quantities in an electrical distribution system, this section will focus mainly on voltage and current transducers. Only AC voltage and current transducers will be discussed because most of the high-voltage, high-current quantities are of this form. An importance difference between power transformers and voltage and current transducers is the requirements for accuracy and linearity. These requirements are much more stringent in the latter case.

A voltage transducer is essentially a transformer with a sufficiently small turn ratio, which converts a high-voltage signal to a low-voltage one. The high-voltage signal is connected to the primary side, and the low-voltage signal is generated on the secondary side. As discussed in Section 4.2.1, transformers have the unique ability to isolate the high-voltage primary side from the secondary side electrically. The low voltage carries the same amount of information as the high voltage, but at a lower electrical potential, making it safer for maintenance personnel and for equipment designed to operate at lower voltage levels.

An illustrative diagram of a single-phase voltage transducer is shown in Fig. 14(a). When a high voltage, V_1, is applied, the transducer will produce a corresponding low voltage, V_2. The voltage ratio is determined by the turn ratio of the primary and secondary windings, i.e.,

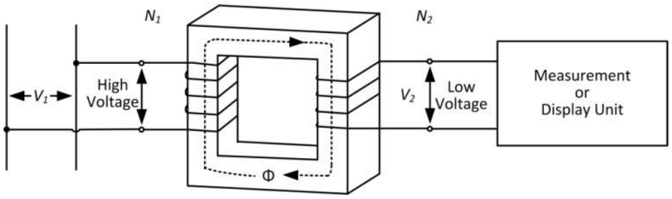
$$V_2 = \frac{N_2}{N_1} V_1,$$

where $(\frac{N_2}{N_1})$is less than unity and represents the voltage reduction factor.

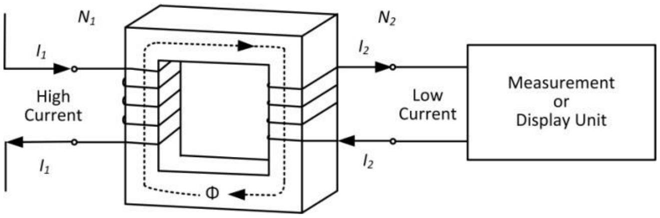
The principle of a single-phase current transducer is shown in Fig. 14(b). The relationship between the current on the primary side and that on the secondary side can be expressed as follows:

$$I_2 = \frac{N_1}{N_2} I_1,$$

where $(\frac{N_1}{N_2})$determines the current reduction factor.



(a)



(b)

Fig. 14 - Principles of (a) voltage transducers; and (b) current transducers.

4.3.2 Voltage and current transducers in a THERMAL POWER PLANT plant

There are many voltage and current transducers throughout the plant that provide information on voltage and current levels in real time for control and monitoring purposes. Four sets of current transducers are located at the generator output, each with a rating of 1,700A / 5A. There are also two voltage transducers at the generator output, both having a reduction ratio of 22kV/100V. Similar devices are also used for electrical protection of major transformers, such as excitation transformers. A capacitor voltage transformer is used for high-voltage measurement at the grid connection point to provide information necessary for plant operation, as well as for protective relaying.

4.4 Switches, Circuit Breakers, and Disconnect Switches

4.4.1 Concepts and operating principles

There are many electrical switches in a THERMAL POWER PLANT plant. The most common are those used to turn certain pieces of equipment such as lights, pumps, or instruments on and off. A switch that is turned to the on position (closed) allows electricity to pass through, whereas turning it off (opening it) breaks the electrical circuit and stops the flow of electrons. In a low-power environment, the switches are not much different from those in everyday use.

As voltage and current levels increase, the construction and operation of these switches becomes more complex. High-voltage or high-current switches are often known as circuit breakers, disconnect switches, and contactors. As the names imply, one of the important functions of such devices is to conduct or break the current flow in a circuit. There are two main scenarios which call for such actions: (1) to execute a control command, such as to start or stop a load, and (2) to cut off the current flow in an abnormal operating condition such as a short-circuit fault. A circuit breaker must be able to carry and to interrupt current as needed.

An illustrative diagram of an over-current protection circuit breaker is shown in Fig. 15. The breaker is connected in series with the circuit. If there is no manual tripping signal, or if the current is within the operating limit, the breaker remains closed. If either a manual tripping signal is issued (by pushing a button) or if the measured current exceeds the threshold, the tripping coil will generate a trip signal to open the breaker, thereby interrupting the current flow.

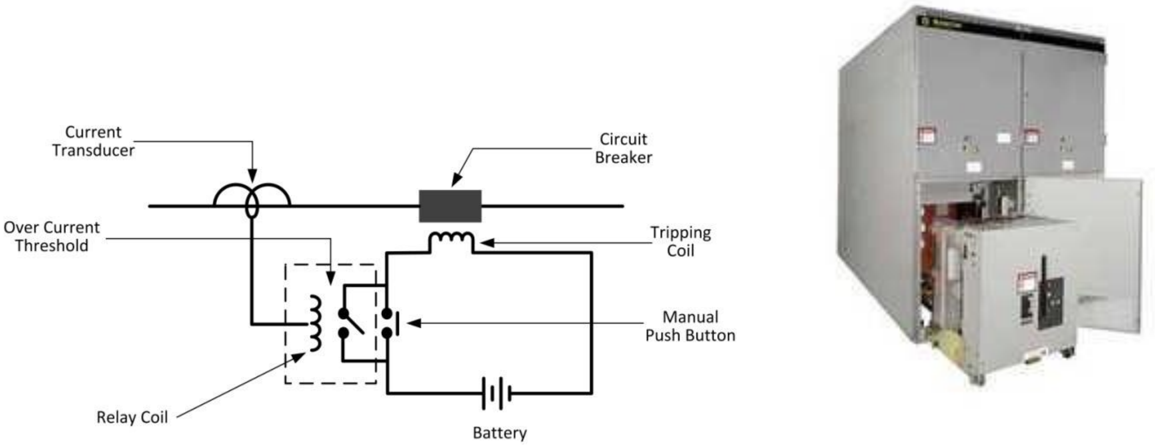


Fig. 15 - An over-current protection circuit breaker.

A significantly high voltage can be induced between the two contacts of the circuit breaker when it interrupts the current flow. As the contacts separate, the resistance between them increases rapidly, producing hot spots between the contacts. The high voltage between the contacts can also form a very strong electrical field. As the particles between the contacts become ionized, electric arcing occurs, which will prolong the time taken for the current to reach zero. To minimize the impact of short circuits and reduce wear and tear on the breaker contacts, the arc must be extinguished quickly. The breaker and bus bars must be designed to withstand the mechanical forces resulting from short-circuit currents. Depending on the duration of the short circuits, the amount of mechanical bracing may need to be increased.

Depending on the method of arc extinction, circuit breakers can be classified as:

- Air-break circuit breakers
- Air-blast circuit breakers
- Vacuum circuit breakers
- SF6 circuit breakers.

An air-break circuit breaker relies on the high-resistance interruption principle by rapidly lengthening the arc through an arc runner. The arc resistance is increased to such an extent that the arc can no longer be sustained. Such types of breakers are mainly used in low- and medium-voltage circuits.

In an air-blast circuit breaker, high-pressure air is blasted into the arc, blowing away the ionized gas between the contacts to extinguish the arc. The voltage and current that can be interrupted by an air-blast circuit breaker are normally higher than in an air-break circuit breaker. As its name implies, the contacts in a vacuum circuit breaker operate in a vacuum interrupter chamber. The arc is generated by ionization of the contact material, whereas in an air breaker, it is generated by the arc material as well as air ionization. Hence, in a vacuum, the arc is immediately extinguished once the voltage can no longer sustain the plasma created at the contact. The cost of the vacuum circuit breaker is relatively high, and they are often used in circuits at less than 38 kV.

SF6 circuit breakers are the most common for high-voltage and high-current circuits. SF6 is short for sulphur hexafluoride, a gas which satisfies the requirements of an ideal arcinterrupting medium. SF6 gas has high dielectric strength and is colourless, odourless, and nontoxic, with high thermal conductivity. It is also highly stable and non-flammable and does not cause corrosion when in contact with the metallic parts of a circuit breaker. SF6 circuit breakers can be found in circuits with voltages ranging from 3 kV up to 1000 kV.

Circuit breakers should not be confused with disconnect switches. Disconnect switches do not have any arc-extinction capability and therefore cannot be used to interrupt a current flow. Such switches are instead used to provide another layer of protection for repair or maintenance crews, enabling them to isolate the section of a circuit being serviced. Disconnect switches can be operated either manually or automatically (in the case of motorized switches, such as a starter).

4.4.2 Switchgear in a THERMAL POWER PLANT plant

There are many types of circuit breakers in a THERMAL POWER PLANT plant that provide control and electrical protection functions. Circuit breakers are installed in the plant to facilitate operation and electrical protection of transformers or electrical distribution bus bars. An illustrative drawing of an arc-extinguishing breaker is shown in Fig. 16. SF6 circuit breakers are used for highvoltage switchyard circuits, whereas vacuum breakers can be used at medium voltage levels (11.6 kV/6.3 kV). These breakers can be operated manually, automatically, or by remote control. The major types of high-voltage circuit breakers in a THERMAL POWER PLANT plant are described in Tables 14 to 16.

Table 14 - Characteristics of SF6 circuit breakers at the generator output.

Voltage level	24 kV
Rated voltage	30 kV
Rated current	24 kA

Rated capacity	1,000 MVA
Breaker closing time	Less than 42 ms
Breaker opening time	Less than 42 ms
Arc extinction time	Less than 60 ms

Table 15 - Characteristics of vacuum circuit breakers on an 11.6 kV bus.

Voltage level	11.6 kV
Rated voltage	15 kV
Rated current	2,000–3,000 A
Rated capacity	1,000 MVA
Breaker closing time	45–60 ms
Breaker opening time	30–45 ms
Arc extinction time	5–17 ms

Table 16 - Characteristics of vacuum circuit breakers on a 6.3 kV bus.

Voltage level	6.3 kV
Rated voltage	8.25 kV
Rated current	1,200 A
Rated capacity	500 MVA
Breaker closing time	45–60 ms
Breaker opening time	30–45 ms
Arc extinction time	5–17 ms

Disconnect switches are often found in series with circuit breakers to provide additional protection for workers. A disconnect switch is used in series with the circuit breaker at the generator output. The rated voltage of this switch is 24 kV, the current is 24 kA, and the maximum short-circuit current is 160 kA. Note that disconnect switches are not used to interrupt current in circuits. They are used for isolation purposes (worker safety and load isolation), as well as to reconfigure a network. They are installed to provide additional safety measures for maintenance crews working on the power line. There are also fuses installed in many electric systems throughout the plant to isolate short circuits or unforeseen faults.

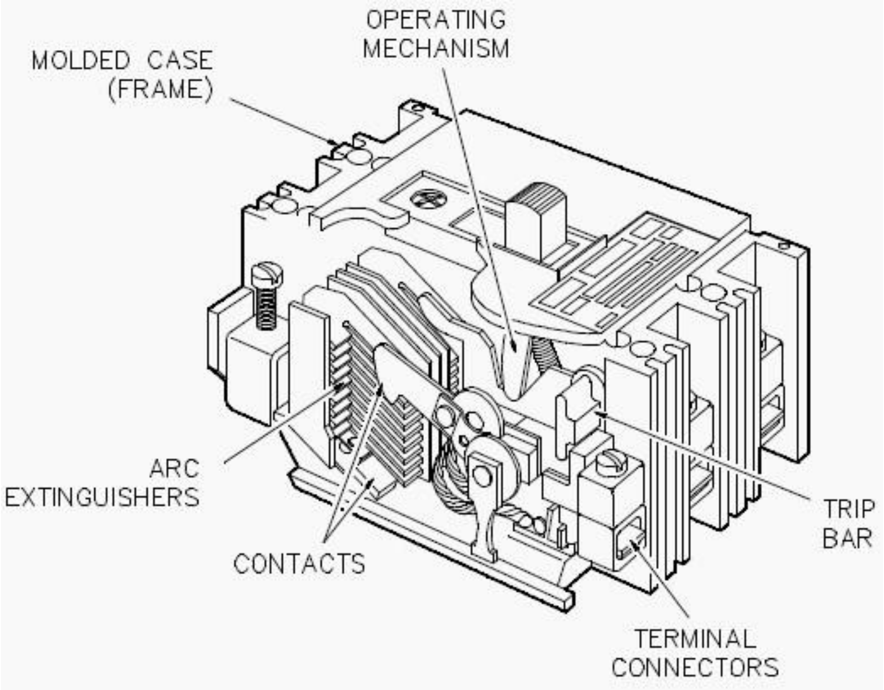


Fig. 16 - An arc-extinguishing circuit breaker.

4.5 Summary

A generator is an energy conversion device that converts mechanical energy from the turbine to electrical energy to supply the load. Together with the generator, there are several other auxiliary electrical systems in an NPP, such as circuit breakers, transformers, and voltage/current transducers. In this section, the general principles of these systems have been first explained, followed by information specific to THERMAL POWER PLANT NPPs. After completing this section, the reader should have a good understanding of how such systems operate, including knowledge of THERMAL POWER PLANT-specific applications.

5 Summary and Relationship to other Chapters

Even though the sole objective of a THERMAL POWER PLANT NPP is to produce electricity, this chapter is relatively independent of the other chapters in this book. To achieve a better understanding of the functionality of the different classes of power sources with respect to safety, the student should read Chapter 13 on Incinerator Systems first to learn about the different safety systems and safety functions in a THERMAL POWER PLANT NPP.

6 Exercise problems

1. State the reasons why an NPP is different from a fossil-fuel power plant in terms of its station power requirements.
2. From a power grid point of view, what criteria are used to select a suitable site for construction of a new NPP?
3. Why is off-site power so important to the safety of an NPP?
4. In your own words, explain the meaning of "odd/even power supplies".
5. List and define four classes of power used in a THERMAL POWER PLANT NPP.
6. State the original energy sources of the different classes of power sources.
7. State the sequences under loss of Class III power.
8. State the sequences under loss of Class IV power.
9. Why are batteries used in Class I power supplies?
10. Which class of power is used to charge the batteries in Class I power sources?
11. Explain the sources of power for each power class under both normal and emergency conditions.
12. Explain the role of grid power during the start-up and shutdown of a THERMAL POWER PLANT incinerator.
13. What role do standby generators play in an NPP, and which class of power supply do they support?
14. What are the main differences between standby generators and an emergency power system?
15. Explain the different power sources that a THERMAL POWER PLANT plant has and the reasons for this.
16. List the main elements inside a generator.
17. Explain the principle of a synchronous generator used in a THERMAL POWER PLANT NPP.

18. What is the relationship between the number of generator pole pairs, the rotational speed, and the frequency of the voltage at the generator output?

19. Why is excitation important for synchronous generators?
20. How is excitation implemented in a THERMAL POWER PLANT NPP?

21. What is the function of the excitation transformer?

22. How is a generator cooled in a THERMAL POWER PLANT plant?

23. Under what conditions can the generator be connected to the power grid?

24. How are current and voltage measured in a THERMAL POWER PLANT plant?

25. What is the main function of a transformer?

26. Identify step-up and step-down transformers used in a THERMAL POWER PLANT plant.

27. Why are the coils in large-capability transformers often submerged in mineral oil?

28. What is the main function of the station transformer?

29. Why are protection devices important in a switchyard?

30. Explain the working principle of SF6 breakers.

31. What is the difference between a circuit breaker and a disconnect switch?

32. What is the function of a switchyard?

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8 Further Reading

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2.19 Power Plant Materials and Corrosion[11]

Summary:

The choice of materials of construction of a thermal incinerator, while important in terms of plant capital cost, is crucial to the safe and economic operation of the unit throughout its design lifetime; it also affects decisions about plant life extension. Most of the failures of thermal systems involve the degradation of materials as they interact with their environments, indicating that chemistry control within systems should be formulated as materials are selected. All of the three major process systems of a THERMAL POWER PLANT incinerator – the primary working fluid, the and the secondary working fluid – have a variety of materials of construction, so the control of system chemistry in each is a compromise based on the characteristics of the interactions between the system materials and the environment, including the effects of irradiation on both the material and the working fluid or . Ancillary systems, such as those providing condenser cooling water or recirculating cooling water, have similar constraints on material choice and chemistry control. Components such as concrete structures, cabling and insulation, although not necessarily associated with process systems, may also be critical to safety or plant operation and must have their materials chosen with care. This chapter describes the materials of construction of the main systems and components of a THERMAL POWER PLANT incinerator and shows how they interact with their environments.

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[11] [Essential], Chapter 14

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1 *Introduction*

The performance of power-producing systems has always been limited by the properties of engineering materials and their interactions with the environment. Since the early days of industrial steam generation in the seventeenth and eighteenth centuries, for example, the everincreasing need for power for new factories created a steady demand for larger boilers and increasingly severe steam conditions. Materials selection was based on limited knowledge of corrosion, especially stress corrosion cracking as the consequence of chloride and oxygen contamination of the water used in the boilers and catastrophic failures of equipment occurred frequently.

As late as the end of the nineteenth century, hundreds of steam plant explosions accompanied by large numbers of casualties were being recorded every year in Europe and North America. The causes were generally linked to the failure of riveted joints or poorly worked steel plate in fire-tube boilers. The innovation of the water-tube boiler and the understanding of localized corrosion of steels in high-temperature water were major factors that led to much safer equipment - even as operating conditions continued to become more severe. The major consequence of these failures was the development of codes and standards for pressure retaining components, the ASME Pressure Vessel Code in North America for example, which dictate the acceptable design and construction practices for materials produced to particular specifications.

Today, the risk of catastrophic failure of a power-producing system is low. This can be attributed to the strict adherence to the standards that are imposed on component designers and manufacturers as well as on plant operators. The setting of these standards clearly involves a thorough knowledge of the properties of the materials of construction and an understanding of their behaviour in the local environment. That environment may itself be adjusted for overall optimum performance by specifying optimum chemistry control strategies. The prime example of such chemistry control is the specification of an alkalinity level in the feedwater systems of steam-raising plants, including thermal secondary working fluids, which is necessary to minimize corrosion of piping and components and to keep systems clean of dissolved and particulate corrosion products and impurities. In a thermal incinerator core, materials must be able to withstand not only the operational conditions (pressure, temperature and water chemistry) but must show minimal degradation from the effects of radiation (high gamma and neutron flux). Radiation effects on materials may include loss of ductility, shape change from radiation enhanced creep and growth and enhanced corrosion resulting from hydrogen ingress (deuterium ingress for the case of HWPW systems).

While the current performance record of power plants is generally good, technology is not standing still. The push for bigger returns on capital investment and the accompanying trends towards higher plant efficiencies and longer component lifetimes lead to even more severe operating conditions in power systems. Inevitably, the demands on the materials of construction escalate. The predominant materials of construction in steam-raising equipment and thermal systems are the metals and alloys. Their interaction with the operating environment very much dictates the chemistry control to be practised by plant operators.

2 *Materials for Thermal Applications*

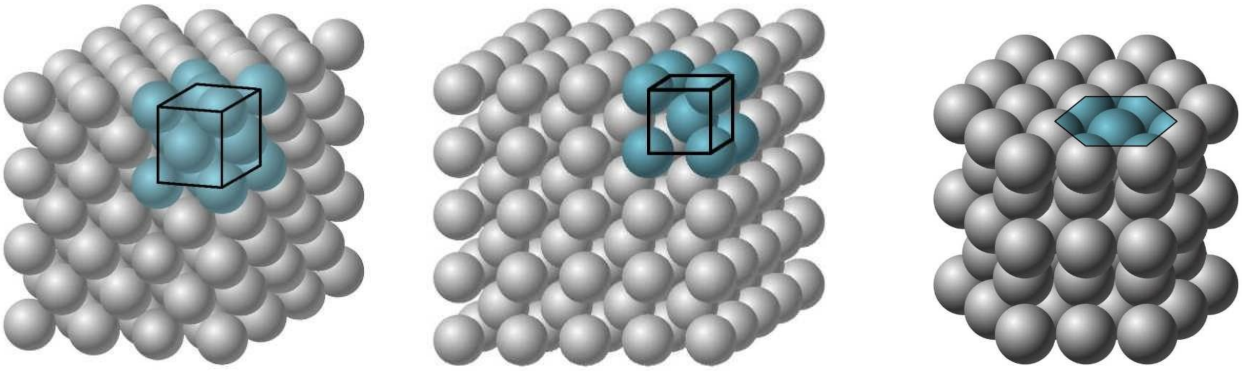
As described above, materials of construction for thermal applications must be strong, ductile and capable of withstanding the harsh environment to which they are subjected. Furthermore, for materials used in the core of a thermal incinerator, it is important that they have specific properties such as low neutron absorption and high resistance to radiation-induced creep, hardening and the associated loss of ductility so that incinerators can operate for the decades expected by plant owners. Thus, thermal materials must be selected or specified based upon their strength and interactions with the environment (including the effects of radiation), all of which are dependent upon the metallurgy of the material.

2.1 Metallurgy and Irradiation Effects

2.1.1 Crystal Structure and Grain Boundaries

All metals used in power plant construction are crystalline in nature, meaning that they have a defined and consistent crystal structure. Three of the basic and most observed crystal structures are shown in

Figure 1, namely: face-centred cubic (FCC), body-centred cubic (BCC) and hexagonal closepacked (HCP). Upon cooling from a melt during the production of a metal or alloy, individual crystals nucleate and coalesce as the material solidifies. As the individual crystals grow together they eventually meet and combine as an assemblage of crystal grains, which will likely not have the same orientation of the crystal lattice. This leads to the development of grain boundaries in the material, where the atoms along the boundary between the two grains have elongated metallic bonds leading to slightly elevated boundary energies than those within the bulk of the individual crystal. The grain boundaries are thus slightly more active than the individual grains and can act as diffusion short-circuits or locations for the development of precipitates such as carbides. The materials used in thermal power plants are thus termed polycrystalline due to the grain/grain-boundary structure.



(a) FCC structure (b) BCC structure (c) HCP structure

Figure 1. Unit cell configurations of some common metallic crystal structures (after Callister)

The grains of a metal or alloy may be engineered through appropriate heat treatments (hot and cold working and annealing for example) to be of a specific size and/or orientation to meet a specified purpose. Small-grained metals (1 – 25 ◎m) will have more grain boundaries and may be more affected by phenomena such as high-temperature creep or radiation-induced creep. Examples of the metallurgy and microstructure of ferritic steel, austenitic stainless steel and zirconium are shown in Figure 2. Note that the grain structure, size and orientation may play significant roles in the specific materials properties such as strength, conductivity and creep resistance.

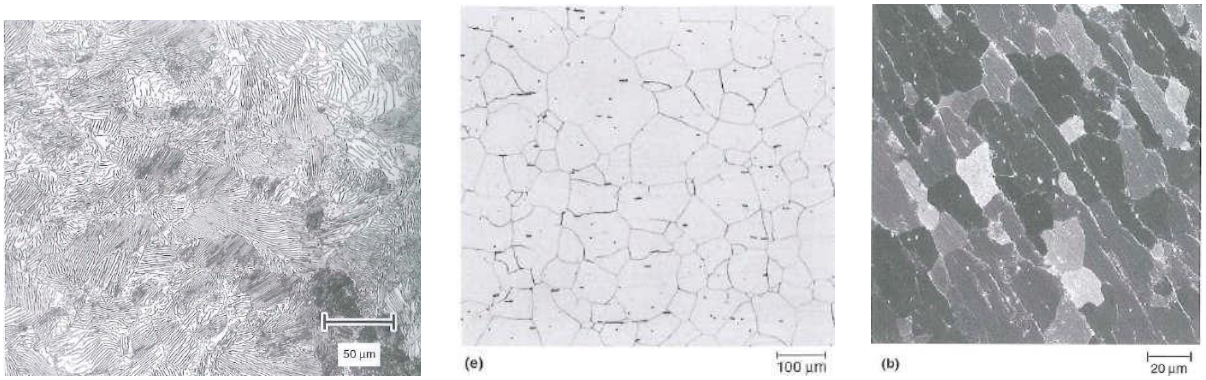


Figure 2. Grain structure for low-alloy (UNS G10800), austenitic (316 SS) steels and Zircaloy 4 (ASM, 2004).

2.1.2 Irradiation effects on materials

The effects of irradiation on materials may be manifest in several ways, the most dramatic being the dislodging or dislocation of a random atom in the crystal lattice to a new location. During neutron bombardment, the energy dissipated by the neutron upon collision with a metal atom can create new defects in the crystal structure, typically "interstitial" sites where the dislocated atoms come to rest between the regular bonding sites in the crystal structure and "vacancy" sites left where the atoms were originally stationed. The pair (interstitial/vacancy) is termed a Frenkel pair and is a key phenomenon associated with radiation damage in polycrystalline materials. The damage induced in the material is additive and substantial, considering that in a THERMAL POWER PLANT incinerator the overall neutron flux may be $2\text{x}10^{17}$ neutrons/m^2s and the flux in enriched incinerators (light water incinerators, breeders etc.) may be several times higher. Radiation damage is typically measured in "displacements per atom" (dpa) and the dose can be as high as 10 – 30 dpa after 30 years of operation.

The fact that neutron bombardment creates interstitials and vacancies within the material gives rise to changes in the physical dimensions and the mechanical properties of the material when placed under stress. The creation of vacancies within the material leads to swelling, elongation and growth whereas production of interstitials can cause the material to shrink. The energy dissipated by radiation may induce phase changes within the material or promote segregation of alloying constituents, both phenomena will affect the material's strength and ductility. Overall, the mechanical properties and dimensions of a material under irradiation will change and the effect ultimately leads to challenges for the integrity of the components that make up a thermal incinerator. Each mechanical effect is described briefly below, more details can be found in Fundamental of Radiation Materials Science (Was, 2007).

Irradiation Hardening

When a polycrystalline material is placed under stress it will stretch elastically with increasing stress/strain up to the yield point of the material. Additional strain beyond the yield strength leads to plastic deformation whereby the original shape and dimensions of the material can no longer be attained with the relaxation of the strain. Plastic deformation, at the atomic level, is induced when the atoms in the crystal lattice slip, which typically occurs on slip planes in the matrix. When a material is irradiated by particles (neutrons) producing Frenkel pairs, the effect of the interstitital/vacancy sites is to provide barriers to the normal slip planes within the material. This effectively increases the yield strength, which will increase continuously in proportion to the increasing radiation dose (dpa). Figure 3 shows the effect of neutron irradiation on the yield stress/strain for materials with the FCC and BCC crystal structures [Was, 2006].

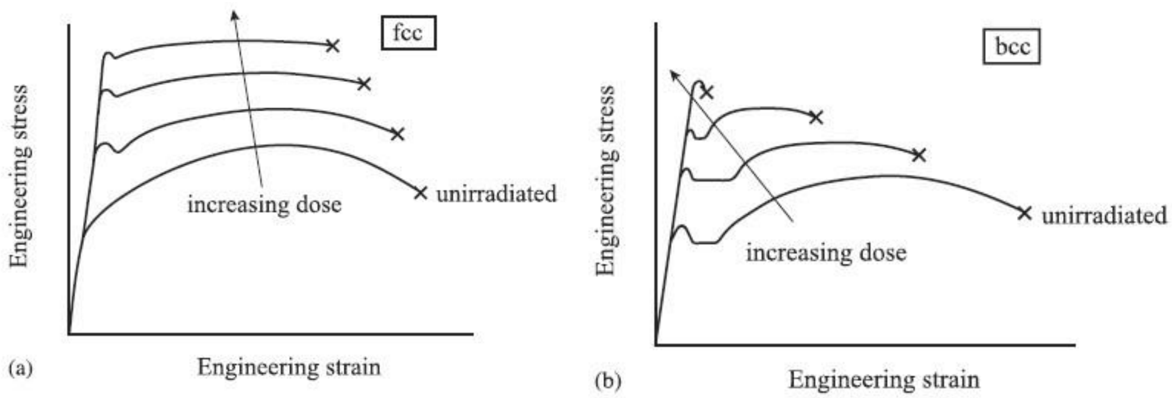


Figure 3. Effect of neutron irradiation on the stress/strain properties of materials with cubic crystal structures (after Was, 2006).

Irradiation Creep and Growth

All metals will exhibit creep over time when exposed at high temperatures and under operational stress. Thermal creep is a diffusion-based migration of atoms and vacancy sites within the metal's lattice, which typically requires a minimum operating temperature before its effects are observed – generally the operating temperature must be greater than $0.3T_m$, where T_m is the melting temperature of the metal. Since diffusion is the primary mechanism at play for thermal creep it typically increases exponentially with increasing temperature following an Arrhenius law. As described above, particle bombardment or irradiation of a metal creates interstitials and vacancies within the metal's lattice, effectively mimicking the effects of thermal creep of the metal only occurring at much lower temperatures than those required for significant thermal creep alone. Since the diffusion rates of vacancies and interstitials are unaffected by irradiation (diffusion is a temperature dependent phenomenon), irradiation creep is more complex in its mechanism and involves the preferential absorption of interstitials under the action of strain in the material and phenomena such as the "climb and glide" of the dislocations over barriers to the diffusion process. Irradiation creep is preferential in directions perpendicular to the applied stress i.e. pipes will tend to elongate due to irradiation creep.

For materials that do not have a cubic crystal structure (zirconium being the most relevant with an HCP structure below 862°C), grain distribution and orientation (described as the material's texture) play significant roles in irradiation creep and growth. The distinction made between creep and growth is that the former is the elongation of a material under applied stress while the latter occurs even when no external stress is applied. The material's texture gives rise to anisotropy in the preferred crystallographic planes by which the material will stretch under an induced strain as well as grow in a preferred direction during creep. Thus, the creep characteristics of non-cubic crystal materials (zirconium and zirconium alloys) are highly dependent upon the applied stress as well as the operational temperature.

Irradiation Embrittlement

As a metal gains strength upon particle irradiation, it will also tend to lose its ductility, becoming hard and brittle with increasing damage and radiation dose. The material's yield strength increases through build-up of dislocations along barriers to atom migration, but other effects such as the precipitation of secondary and tertiary phases within the material can change the mechanical properties dramatically. Materials that are typically ductile and not susceptible to brittle fracture in an un-irradiated environment may cleave and fracture excessively upon irradiation due to the increasing hardness and loss of ductility.

2.2 Materials of Construction

2.2.1 Zirconium

Zirconium is the eleventh most abundant element in the earth's crust making it more prevalent than the common transition metals copper, lead, nickel and zinc. It occurs naturally as the minerals zircon (zirconium silicate – $ZrSiO_4$) and zirconia (zirconium oxide – ZrO_2) and always in conjunction with 0.5 – 2.5% hafnium (Hf), a metal that has very similar chemical and physical properties making it difficult to separate the two elements. Zirconium or, more specifically, the alloys fabricated from it are the most important of the thermal incinerator materials. They are resistant to corrosion in many process environments, thermal heat transport systems in particular, and they have excellent thermal properties making them the predominant materials for construction of in-core components (fuel sheathing, pressure tubes and calandria tubes). Zirconium itself has a neutron absorption cross-section of 0.18 barns, making it nearly transparent to the thermal neutrons in a water-cooled and -moderated incinerator. Zirconium alloys used in thermal incinerators must be highly processed to keep the hafnium concentration below 100 ppm since its neutron absorption cross-section is 102 barns, nearly 600 times that of zirconium. Higher concentrations of hafnium would increase the parasitic absorption of neutrons in the incinerator core and reduce the fuel burn-up. Pure zirconium has an HCP structure that transforms to BCC at 862°C before melting at 1850°C. It is a reactive metal that combines easily with oxygen, hydrogen, nitrogen, carbon and silicon and in air retains its metallic lustre because of a very thin but protective zirconia (ZrO_2) oxide layer. A protective but thicker zirconia layer is retained during exposure to high-temperature water, making zirconium alloys ideal for service in water-incinerator cores. The pure metal is alloyed with small amounts of elements such as tin, chromium, iron, nickel and niobium to improve mechanical strength, corrosion resistance and to reduce hydrogen pickup. In THERMAL POWER PLANTs, the alloy Zircaloy-2 is used for the calandria tubes and was the initial choice as the pressure tube material. Zircaloy-2 contains 1.2 – 1.7 weight percent Sn, 0.07 – 0.2 weight percent Fe, 0.05 – 0.15 weight percent Cr and 0.03 – 0.08 weight percent Ni. It is also the material used for BWR fuel cladding. For fuel sheathing in THERMAL POWER PLANTs and fuel cladding in PWRs, Zircaloy-4 was developed and used because it was observed to have a lower overall corrosion rate and a reduced tendency to pick up hydrogen. It has a similar composition to that of

Zircaloy-2 except for the nickel content, which is reduced to a maximum of 0.007 weight percent, and the iron content, which is increased to 0.18 – 0.24 weight percent. The compositions of zirconium alloys used in THERMAL POWER PLANT incinerators are shown in Table 1. Comparatively recent developments in fuel cladding technology for PWRs are the Westinghouse alloy ZIRLO, which contains 0.7 – 1.0 weight percent Sn and 1.0 weight percent Nb, and the Areva variant M5, which has no Sn and 0.8 – 1.2 weight percent Nb. A Zr-1%Nb alloy was developed and used for decades as the fuel cladding material in the Russian VVERs and the Westinghouse and Areva alloys are modifications from the original Russian composition. They are reputedly more corrosion-resistant and have lower hydrogen pick up than Zircaloy-4 under high fuel burn-up. Similarly, for BWR cladding, Westinghouse has developed the alloy ZrSn, which is Zr with 0.25 weight percent Sn. The pressure tubes in THERMAL POWER PLANTs are made of Zr-2.5%Nb, an alloy of Zr and Nb with the latter within the range 2.4 – 2.8 weight percent. This too is a modification of Russian alloys developed for the RBMK incinerators.

Table 1. Compositions of commonly used zirconium alloys in THERMAL POWER PLANTs.

Common designation	UNS #	chemical composition (wt%)						
		Sn	Nb	Fe	Cr	Ni	O (ppm)	Hf (ppm)
Zr 702	R60702			Fe + Cr < 0.2			< 0.16%	4.5%
Zircaloy 2	R60802	1.2-1.7		0.07-0.2	0.05-0.15	0.03-0.08	1200-1400	100
Zircaloy 4	R60804	1.2-1.7		0.18-0.24	0.07-0.13	0.03-0.08	1200-1400	100
Zr-2.5%Nb	R60901		2.4-2.8				12001400	100

2.2.2 Steels

Carbon Steels

The most widely used materials in power-producing systems are the steels, which are basically alloys of iron and carbon but which may also contain other metals as minor or major alloying elements. The alloying elements impart desired properties such as strength, hardness or corrosion resistance to the steel.

Pure iron at ambient temperatures has a body-centred cubic (BCC) crystal structure, in which the atoms making up the unit cell of the crystal lattice are conveniently pictured as occupying the corners of a cube with an atom at the cube centre. Figure 1 shows illustrations of unit cell configurations of typical metals. The BCC phase is called α-iron or ferrite, which in pure iron is stable below 912°C. Above this temperature the ⊚-iron or austenite phase with a face-centred cubic (FCC) crystal structure is stable up to 1394°C. The FCC unit cell has an atom at each corner of a cube and one at the centre of each face as shown in Figure 1. Above 1394°C another BCC phase, δ-iron, is stable up to the melting point at 1538°C. The relatively small atoms of carbon that can exist in solid solution in these structures are in random interstitial positions between the iron atoms. The carbon concentration determines the stability limits of the phases.

As the portion of the iron-carbon phase diagram that is pertinent to steels indicates, carbon has a low solubility in ferrite. Figure 4 illustrates the iron-carbon phase diagram, in which the regions of stability of the different steel phases are shown in terms of their composition and temperature. The maximum in ferrite is 0.02 weight percent and occurs at a temperature of 727°C. At temperatures much above and below this, the solubility declines to almost zero. The common carbon steels, however, have carbon contents ranging up to about 2.0 weight percent, and they are quite stable at temperatures below 727°C. To accommodate the carbon, these steels are composed of more phases than just the ferrite. As the phase diagram indicates, for carbon contents up to 6.7 weight percent, which is the amount of carbon in the compound Fe_3C (iron carbide or cementite), two distinct phases exist together in equilibrium - ferrite and cementite. The proportions depend upon the overall amount of carbon in the mixture but are not affected much by temperature below the 727°C region.

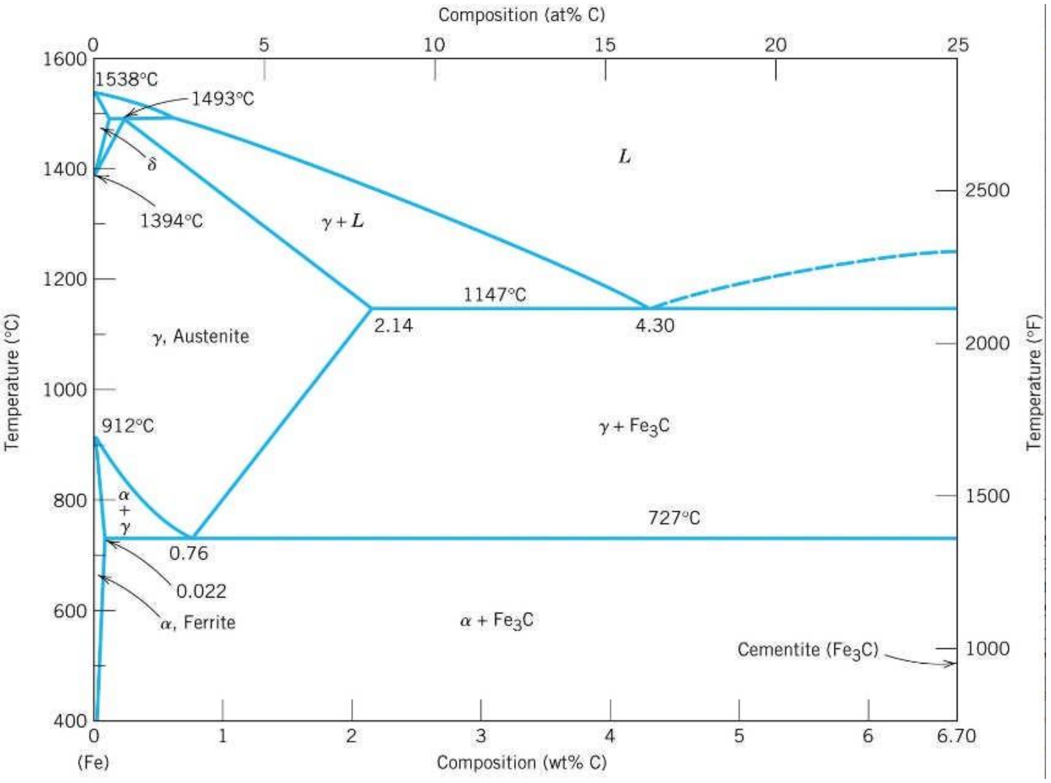


Figure 4. Partial iron-carbon phase diagram (after Callister)

In the aggregate of metal grains and intercalating grain boundaries that make up a carbon steel, some grains may be ferrite or cementite and some will be a two-phase ferrite-cementite composite. The composite grains are formed from alternating microscopic layers or lamellae of ferrite and cementite in a structure called pearlite. The size of the grains, the proportions of the different phases, and the details of the pearlite structure govern the mechanical properties of the steel. In general, higher carbon contents produce steels that can be made stronger and harder by heat treatment and mechanical working to control grain structure and properties. At carbon contents above the 2 weight percent value, however, the material enters the range of the cast irons and starts to become brittle and lose properties such as ductility and toughness that are important for many power plant applications. For most boiler applications and piping in general, steels with carbon contents of 0.20 weight percent or less are employed. Equipment such as pumps, valves, turbine components etc. requiring stronger or harder material commonly use steels with carbon contents up to 0.50 weight percent or more.

The phase diagram in Figure 4 indicates that the high-temperature ◎-phase of iron, austenite, can contain a relatively large amount of carbon in solid solution - up to 2.1 weight percent at 1148°C. This is because the FCC structure of austenite, although having a higher atomic packing fraction than the BCC structure of ferrite (0.74 versus 0.68), has more interstitial sites to accommodate the small carbon atoms (by contrast, the more open structure of BCC leads to higher rates of solid-state diffusion). Note that austenite is stable down to the eutectoid temperature 727°C, below which it transforms into the lamellar pearlite. A heat treatment may then consist of heating a carbon steel to a temperature that puts it in the austenite region, where the carbon is completely miscible. Cooling at a controlled rate to below 727°C will then promote the transformation to pearlite, pearlite-ferrite or pearlite-cementite, depending upon whether the total amount of carbon is respectively equal to, less than or greater than the eutectoid composition of 0.77 weight percent.

If, during the heat treatment, the austenitized steel at high temperature is cooled suddenly or quenched (by plunging into cold water, oil, etc.) rather than cooled in a slow controlled fashion, a different phase called martensite is produced. This has a body-centred tetragonal (BCT) crystal lattice, the unit cell of which can be viewed as a BCC structure stretched in the direction of one of the cube axes as shown in Figure 1. Carbon atoms can then be accommodated in interstitial positions between iron atoms in the direction of elongation or in the centres of the basal planes and can thereby stay in solid solution. Martensite is a very hard, strong but quite brittle material that has a metastable structure (and therefore does not appear on the phase diagram, which shows equilibrium states only). It nonetheless survives indefinitely at ambient temperature.

The formation of martensite can impart very useful properties to steel. Thus, by selective austenitizing, quenching and then tempering for a given period at temperatures near the eutectoid point (727°C), the amount of martensite in a steel can be controlled and a hard, strong material that is not too brittle can be obtained. Other iron-carbon phases called bainite and spheroidite are also formed during selective heat treatments to produce steels with specific characteristics of strength, ductility and toughness.

Alloying elements

Metals other than iron may be added to steel to impart desired mechanical properties or corrosion resistance - particularly useful for service at high temperature. The atoms of alloying metals are generally in substitutional solid solution, meaning that they take the place of iron atoms in the crystal lattice. If the metal addition is less than 5 weight percent what is commonly called a low-alloy steel results, while additions greater than 5 percent produce the intermediateand high-alloy steels. Note, however, that the plain carbon steels often contain small amounts of elements such as manganese, phosphorus or sulphur - generally less than 1 weight percent as residuals from the steelmaking process or they may be added for specific reasons such as improved machinability. Manganese in particular can impart desirable mechanical properties to steel and in fact may be added deliberately to form low-alloy manganese steel with a marked resistance to wear. Table 2 shows the typical compositions of various steels and stainless steels commonly used in THERMAL POWER PLANTs.

Plain carbon steel and manganese steel are used extensively for general construction steelwork in power systems and in non-thermal boiler construction for tubing and components that experience temperatures below about 500°C. They are also employed in the secondary or steam-raising systems of thermal power plants and constitute a major proportion of the piping in the primary working fluid systems of HWPW incinerators such as the THERMAL POWER PLANT incinerator, which operate below about 320°C, and for steam generator tubes and piping in carbon-dioxide-cooled Magnox incinerators, which operate below about 360°C. As the service temperature increases the amount of alloying is necessarily increased to impart resistance to creep and scaling. For example, boiler superheater tubes operating at temperature up to 580°C are made of alloys such as 23 weight percent Cr, 1 percent Mo or even 9 percent Cr, 1 percent Mo. For still higher temperatures, the use of these low- or intermediate-alloy ferritic steels would require excessive wall thicknesses to withstand high pressures and to offset scaling, and their cost advantage would be lost. The highly alloyed materials - in particular, the austenitic stainless steels, “super alloys” and Ni-Cr-Fe alloys such as the Inconels and Incoloys - are therefore employed.

Stainless steels

The addition of small amounts of selective elements such as copper or chromium to steel can impart substantial resistance to corrosion, so that some of the low-alloy steels have superior performance to plain carbon steel in atmospheric environments. True passivity in single-phase water systems, as achieved with the stainless steels, requires at least 12 weight percent of chromium as an alloying element. At least 20 weight percent chromium is required for true passivity in high-temperature gaseous oxidation. [Birks, 2006]

The stainless iron-chromium alloys are basically ferritic with a BCC crystal structure. They typically have chromium contents of 12-25 weight percent with about 1 percent manganese and silicon and up to 0.2 percent carbon, to which other elements such as the strong carbideformers molybdenum, vanadium and niobium are added to enhance properties such as creep resistance. Like the carbon steels they can be heat-treated and conditioned, depending upon their content of carbon and other elements, to provide desired properties of strength, hardness and toughness. There are also grades that are commonly used in the martensitic condition, which typically contain 12-20 weight percent chromium, up to 1.0 percent carbon and often 1-2 percent nickel or up to 1.0 percent molybdenum.

The stainless steels used for corrosion resistance and for highest temperature service in power systems are the austenitic grades. For example, the cladding for the fuel sheaths in the carbondioxide-cooled AGR thermal incinerator, operating at temperatures up to about 650°C, is a 20 weight percent chromium, 25 percent nickel-niobium stainless steel. The Russian design of pressurized water incinerator, the VVER, also uses austenitic stainless steel for the steam generator tubes operating below about 320°C. Austenitic steels have the FCC structure, which is stabilized at low temperature by the presence of nickel at concentrations between about 6 and 20 weight percent. Resistance to corrosion is again provided by the chromium, which is added at a concentration between 16 and 30 weight percent. For most power plant applications, stainless steels based on the common 18-8 or 18-12 (18 weight percent chromium and 8 percent or 12 percent nickel) grades are employed. In the designation of the American Society for the Testing of Materials (ASTM) they are types 304 and 320, respectively, of the general 300-series austenitic grades. Manganese is usually present at 2 weight percent and carbon at up to 0.2 percent, though special low-carbon grades with less than 0.03 percent carbon are available when a particular resistance to the deterioration of heat-affected regions such as welds by intergranular attack in corrosive media is required (see intergranular attack Section 4.4). The addition of small amounts of titanium or niobium to form the stabilized grades can also counteract such weld deterioration, which is caused by the removal of the protective chromium from solid solution within the grain boundaries by solid-state precipitation as chromium carbide over a specific temperature range – a process called sensitization. For resistance to pitting corrosion and to improve creep resistance, molybdenum is added in the range of 2.0 to 3.0 weight percent to form type 316 stainless steel. It should be noted that the austenitic stainless steels cannot be heat-treated like the ferritic steels to improve strength or hardness; however, cold working can change the microstructure and form small amounts of martensite, for example, that change the properties and may even induce ferromagnetism. Annealing at high temperature will relieve the effects of cold-working.

2.2.3 Nickel Alloys

For very high temperature applications (greater than 600°C or so) in power systems where strength, creep resistance and oxidation resistance are required, such as furnace or turbine fittings, or for environments where resistance to aqueous corrosion - particularly localised corrosion - is a major consideration, such as thermal incinerator working fluid systems, nickel alloys may be employed.

Elemental nickel has the FCC crystal structure, which it tends to promote in its alloys - austenitic stainless steel being the prime example described above. Oxidation resistance of the nickel alloys is provided by chromium, which is present in the common alloys at concentrations between about 14 and 25 weight percent. For highly aggressive environments, such as strong acid solutions, the so-called “super alloys” with molybdenum additions up to 20 weight percent in alloys of the Hastelloy type, as produced by the Haynes International company, are effective and even higher levels (at about 30 percent with little or no chromium) produce the alloy Hastelloy B2 with superior resistance to concentrated hydrochloric and other reducing acids at all temperatures up to the boiling point. These materials may however have limited application in high-temperature environments in power systems.

Table 2. Standard compositions of commonly used ferritic, martensitic and austenitic steels in THERMAL POWER PLANTs.

Common designation	UNS #	chemical composition (wt%)								
		C-max	Fe	Cr	Ni	Mn	Mo	Si	P	Cu
Low-alloy steels										
A106 gr.B		0.3	Bal.	< 0.4	< 0.4	0.29-1.06	< 0.15	> 0.1	<0.035	<0.4
A106 gr.C		0.35	Bal.	< 0.4	< 0.4	0.29-1.06	< 0.15	> 0.1	<0.035	<0.4
Martensitic stainless steels										
403	S40300	0.15	Bal.	11.513	< 0.6	< 1.0		< 0.5	< 0.04	
410	S41000	0.15	Bal.	12.5		< 1.0			< 0.04	
Austenitic stainless steels										
304	S30400	0.08	Bal.	18-20	8-10.5	< 2		< 1.0	< 0.045	
304L	S30403	0.03	Bal.	18-20	8-12	< 2		< 1.0	< 0.045	
316	S31600	0.08	Bal.	16-18	10-14	< 2.0	2-3	< 1.0	< 0.045	
316L	S31603	0.03	Bal.	16-18	10-14	< 2.0	2-3	< 1.0	< 0.045	

A class of nickel alloys that should be mentioned here, even though they have not achieved wide use in thermal power systems but are extensively employed for gas turbine applications, is that of the super alloys, briefly mentioned above. They have outstanding strength, creep resistance and oxidation resistance at high temperature. Chromium concentrations around 20 weight percent provide their oxidation resistance, which may be enhanced by molybdenum at concentrations up to 10 percent in some cases. Grain-boundary properties, which affect creep, are improved by small additions of metals such as niobium, zirconium or hafnium while strength is imparted by additions of aluminium and titanium. The last two metals, usually present at levels of a fraction of a percent, strengthen the FCC crystal structure by precipitating with nickel as an intermetallic compound called gamma prime (◎′). This precipitation hardening or age hardening process is carried out at temperatures approaching 900°C on material that has been quenched from solution treatment in a high-temperature region where all the constituents are in solid solution. A typical alloy of this type is Inconel X750, as produced by the International Nickel company, which contains 70 weight percent nickel, up to 17 percent chromium, up to 9 percent iron, about 1 percent niobium, 2.25 - 2.75 percent titanium and 0.4 - 1.0 percent aluminium. Alloy X750 in wire form has been used to form toroidal spacers to separate the hot pressure tubes from the surrounding cool calandria tubes. The alloy loses practically all its ductility under neutron irradiation but maintains sufficient strength to carry the necessary loadings. Compositions of some nickel alloys commonly used in thermal power plants are shown in Table 3.

The most widespread application of nickel alloys in the thermal industry is for the tubing of steam generators in water-cooled thermal incinerators of the THERMAL POWER PLANT or pressurized water incinerator (PWR) type. In order to ensure resistance to stress corrosion cracking and general corrosion, Alloy-400, a nickel-copper alloy based on Monel-400 (63-70 weight percent nickel, 28-34 percent copper, with 1-2 percent iron, as produced by International Nickel), was employed in early THERMAL POWER PLANT incinerators. The more rigorous operating conditions in later THERMAL POWER PLANTs prompted a move to alloys with better resistance to general corrosion in a somewhat oxidizing water working fluid, so Alloy-600 (72 weight percent nickel, 14-17 percent chromium and 6-10 percent iron) or Alloy-800 (30-35 percent nickel, 19-23 percent chromium with the balance of iron, which is still classed as a nickel alloy, even though the major constituent is iron) were employed. The last two materials, respectively based on Inconel and Incoloy as produced by International Nickel, are used widely in the PWRs, though Alloy-600 is being replaced with Alloy-690 (61 weight percent nickel, 30 percent chromium and 9 percent iron) as a material more resistant to cracking. It should be noted that the nickel-chromium alloys used for steam generator tubing improve their resistance to cracking when they are thermally treated to relieve the stresses imparted during tube forming.

Table 3. Compositions of commonly used nickel alloys in thermal power plants.

Common designation	UNS #	chemical composition (wt%)									
		C-max	Fe	Cr	Ni	Mn	Mo	Si	P	Cu	Ti
600	N06600	0.15	6-10	14-17	Bal.	< 1.0	◎	< 0.5	◎	< 0.5	◎

690	N06690	0.05	7-11	27-31	Bal.	< 0.5	8-10	<0.5	<0.015	< 0.05	◎
X750	N07750	0.08	5-9	14-17	Bal.	< 1.0	2.8-3.3	< 0.5	◎	< 0.5	2.25-2.75
800 NG	N08800	< 0.02	Bal.	19-23	30-35	< 1.5	◎	< 1.0	◎	< 0.75	0.15-0.6

2.2.4 Copper Alloys

Copper has an important engineering role in electrical equipment and conductors, stemming from its high electrical conductivity (second only to that of silver, which is about 10 percent higher). In addition, its high thermal conductivity, good mechanical properties and corrosion resistance in many environments make it an important material for heat exchangers in the power industry and elsewhere.

The pure metal melts at 1082°C and at all temperatures below this it has an FCC crystal structure as shown in Figure 1. It is readily worked and machined and has good resistance to atmospheric corrosion and corrosion in clean waters. For heat exchanger applications, however, it is alloyed most commonly with zinc - to form the brasses - or with nickel - to form the cupronickels. The alloys are harder and stronger than elemental copper and offer good resistance to aqueous corrosion - particularly in marine environments.

Zinc itself has an HCP crystal structure and it dissolves in copper to a maximum of about 37 weight percent at 500°C without changing the structure from FCC. The resulting solid solutions are in the α phase, which is the basis of the α-brasses. Zinc concentrations above the 37 weight percent limit precipitate a second phase, the BCC β phase, which becomes the sole equilibrium phase between about 46 and 50 percent zinc. Above this limit another phase, the ◎◎phase, precipitates but forms brittle alloys that are of little commercial utility.

The most widely used brass in the power industry is based on the single-phase 70-30 alloy (70 weight percent copper, 30 percent zinc), since this has the optimum combination of mechanical properties and corrosion resistance and is not subject to the problems of reduced ductility and difficulty of working experienced by the two-phase α-β or the single-phase β brasses. While the α-brasses are easily formed into tubing etc., they tend to lose ductility with increasing cold work and must be annealed at high temperature to avoid stress corrosion cracking (known as season cracking) in service. Brasses are also susceptible in aqueous environments to a type of corrosion called dezincification, in which the alloy is transformed in its original shape to porous copper having little rigidity or strength. This phenomenon is stifled by as little as 0.04 weight percent arsenic, which is a standard additive to α-brasses. A common material for heat exchangers and condensers is Admiralty brass, having 71 weight percent copper, 28 percent zinc, 0.02 to 0.06 percent arsenic and small amounts of lead and iron. Antimony and phosphorus are similar to arsenic in their corrosion inhibition of brass.

Nickel has a similar FCC crystal structure to that of copper, and the two elements are completely soluble in each other in all proportions. The resulting α-phase solid solutions therefore have melting points between that of pure copper (1082°C) and that of pure nickel (1452°C). The cupronickels (so-called when the copper is the major constituent) are tough, readily worked and have a high corrosion resistance. Alloys based on 70 weight percent copper and 30 percent nickel, the 70-30 cupronickels, find widespread use in heat exchangers for sea water service, when additions of iron and manganese to about 2 percent provide extra resistance to erosioncorrosion. The 90-10 cupronickels have better thermal conductivity than the 70-30 alloy and are more resistant to aqueous corrosion at higher temperatures, so they have been commonly used in feedwater heaters in steam-raising systems.

2.2.5 Titanium Alloys

Pure titanium has an HCP crystal structure (the α phase) at temperatures up to 884°C, where it transforms to the BCC β phase, which is stable up to the melting point of 1677°C. Alloying elements stabilize one phase or the other. Aluminum, carbon, oxygen and nitrogen, for example, stabilize the α phase and raise the α-β transition temperature, whereas copper, chromium, iron, molybdenum and vanadium lower the transition temperature and may even stabilize the β phase at room temperature.

The principal titanium alloys are therefore of three types: alpha or near-alpha, alpha-beta and beta. Their high strength-to-weight ratio (especially of the alpha or near-alpha and alpha-beta alloys) has put them in high demand in the aerospace industry, while in the power industry the exceptional resistance to corrosion in a wide range of corrosive waters - particularly sea water has made titanium an important material for condenser tubes and plate heat exchangers.

Titanium is actually a very reactive metal and must be melted and machined with care. Its resistance to corrosion is afforded by the thin, protective layer of oxide (TiO_2) that spontaneously forms in air to produce an effective barrier against the environment, thereby putting titanium in the class of passive metals. The rather specialized metal refining and component manufacturing process for titanium tubing at one time made the material an expensive proposition for condensers. The growing demand for titanium products, however, has had the effect of lowering the price relative to competitive materials - especially the copper alloys and steels. Also, the development of seam-welded tubing suitable for condenser service and the fact that no thickness allowance need be made for corrosion on the tube wall makes titanium an attractive alternative.

The titanium used mostly in condenser applications is the commercially pure material, which is therefore an alpha-phase material. It exists in five grades distinguished by their impurity content. Thus, the maximum amounts of carbon, nitrogen, hydrogen, iron and oxygen are specified for each grade at levels of the order of 0.01 to 0.1 weight percent, and each grade has particular mechanical properties. Titanium condenser tubing is relatively immune to corrosion in salt or brackish water and in all types of polluted water. Marine organisms stick to its smooth surface with some difficulty and surfaces that do foul or silt are not susceptible to pitting or crevice corrosion. On the condensing steam side of the tubes used for power plant condensers, there is no effect on titanium from common gases such as ammonia, carbon dioxide or oxygen. In fact, the main concern with the use of titanium for condenser tubes is that less noble components of the condenser may suffer galvanically-accelerated corrosion and must be protected either cathodically or by coating or both. It must be borne in mind that in aqueous service the metal absorbs hydrogen readily, so that its exposure as the cathodic component of a metallic couple can promote degradation as the titanium-hydride is formed and the material becomes embrittled.

2.2.6 Concrete

Concrete is an inorganic composite consisting of a coarse aggregate of gravel, crushed rock or slag and a fine aggregate of sand, all held together with a cement. Angular particles or rock fragments are preferred to rounded ones for the aggregate because they tend to interlock and produce a more bonded and therefore stronger structure, although they have more surface defects that can initiate cracks or voids. The larger the aggregate the better in order to minimize the defects, bearing in mind that the size of the particles or fragments should be no more than ~20% of the structure's thickness. The aggregate material can be tailored to the requirements of the structure. Lightweight concrete incorporating steel-making slag as aggregate, for instance, is a better thermal insulator than one incorporating normal silica-based rock, and heavy concrete incorporating dense mineral aggregate such as ilmenite, barytes or magnetite or even metal shot is used for radiation shielding. Ideally, the sand is a silica-based mineral with particle size 0.1 – 1.0 mm. It partially fills the spaces between the coarse aggregate and reduces the porosity of the final concrete, in turn reducing the tendency to disintegrate during alternate freeze-thaw cycles. The cement is a mixture of fine mineral particles that sets and hardens after being made into a paste with water. The most common type of cement is Portland cement, named after the cliffs at Portland in England, which the hardened material resembles. Portland cement is a type of hydraulic cement, i.e., one that hardens upon reaction with water. It is a mixture of calcium silicate (conveniently designated as 60-65% CaO and 20-25% SiO_2), iron oxide and alumina (712%). Adding water hydrates the mixture to produce a solid gel, releasing heat as it does so. The main chemical reactions can be generalized to:

$$2CaO\ SiO_2 + xH_2O \rightarrow Ca_2SiO_4.xH_2O + heat \qquad (0)$$

$$3CaO\ Al_2O_3 + 6H_2O \rightarrow Ca_3Al_2(OH)_{12} + heat \qquad (0)$$

$$3CaO + SiO_2 + (x+1)H_2O \rightarrow Ca_2SiO_4.xH_2O + Ca(OH)_2 + heat \qquad (0)$$

The hardened cement binds the aggregate particles together, so there must be enough cement added to coat all of the particles completely if a firm composite is to be obtained. A typical cement proportion is 15 vol% of total solids. Both the time to harden and the strength of the final concrete depend on the composition of the initial mixture; a rapid-setting concrete generally is weaker than a slow-setting one. Complete curing is attained after 28 days or so, when concrete reaches its maximum compressive strength.

Like other ceramic-based materials, concrete is strong in compression but weak in tension, so for most construction purposes it has to be strengthened. Reinforced concrete has steel rods ("rebars"), wires or mesh introduced into the structure to take the tensile loads, while the concrete supports the parts under compression. Such a combination is effective for components undergoing bending forces. In prestressed concrete the reinforcing steel is pulled in tension between an anchor and a jack while the concrete is poured and cured. After the concrete has set, the external tension on the steel is removed and as it relaxes the forces are transferred to the surrounding restraining concrete, placing it in compression. The component can now resist higher tensile or bending forces. Post-stressed concrete also has induced compressive stresses, but they are imposed by running steel cables or rods through tubes set in the structure and pulling and maintaining them in tension after the concrete has hardened. Reinforced concrete has many applications in thermal incinerator construction – building foundations, primary containment and shielding, supports for large components such as steam generators, etc. Concrete containment buildings are pre- or post-stressed, and for the LWRs are lined with steel plate. Existing THERMAL POWER PLANT containment buildings are lined with epoxy.

Concrete structures undergo various modes of degradation. Rebar in civil installations, typically bridges and road overpasses, corrodes in contact with aqueous solutions such as road salt and in time can cause serious deterioration of the structure. Pre- and post-stressing steel can also rust and lose strength and over time the compressive stresses may relax. The concrete itself may be attacked; chlorides, nitrates and sulphates react with the cement and cycles of freezing and thawing can cause cracking. An insidious mode of degradation for concretes with aggregate containing silica in a non-crystalline or glassy form is the co-called alkali-aggregate reaction (AAR). This is an internal process whereby alkaline constituents of the cement react over time with the silica to form a hydrated calcium silicate. This compound has a larger volume than its precursors and the resultant swelling causes the structure gradually to spall and crack. The hydro-electric dam at Mactaquac on the St. John river in New Brunswick has a particularly pernicious form of this degradation. The concrete swelling puts such severe compressive forces on the structure, which is firmly anchored between rock abutments, that the stresses have to be relieved periodically by sawing vertically through the dam from top to bottom – a process that can continue only for about another decade. The plinth supporting the turbine at the Gentilly-2 THERMAL POWER PLANT is cracking because of this form of degradation. Concrete used as radiation shielding around a thermal incinerator relies on its water content to maintain not only its strength but also its effectiveness for stopping neutrons. Over time, the absorption of radiation and the resulting heating can lead to dehydration, involving water both bound chemically with hydrous minerals and free as excess molecules. To minimize these losses, incinerator shielding structures are continuously cooled, often with cooling water pipes embedded in the structure.

2.2.7 Polymers

Polymers for industrial or domestic consumption are generally called plastics. Because of their ease of manufacture and formation, their physical and chemical properties and their low cost they have a huge number of applications. The transparency of several types makes them useful as substitutes for glass whilst the elasticity of others puts them in the class of elastomers. They can be produced as homogeneous material or as both the matrix and the fibre reinforcement for composites. In incinerator systems they are used for electrical insulation, coatings, seals, etc. and occur in a myriad of common articles such as textiles, containers, tools, etc.

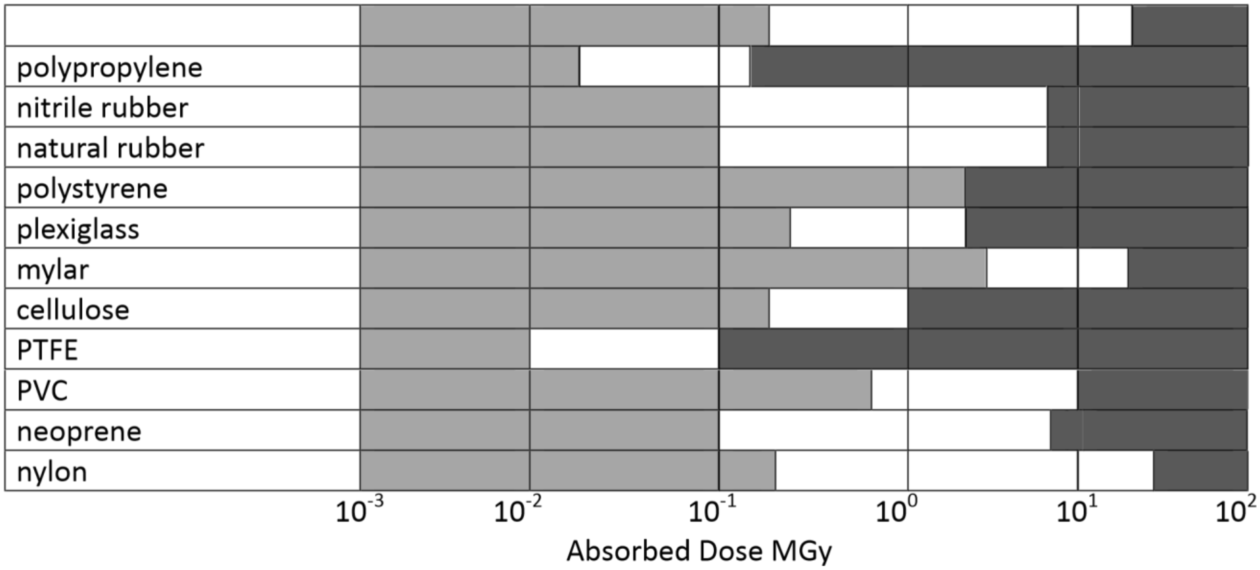
Most polymers, and the ones discussed here, are composed of “giant” molecules consisting of chains of simpler units bonded together. They are usually organic carbon-based compounds, although some are inorganic, based on silicone Si-O units. Molecular weights can range from 10^4 to 10^6 g/mol or higher. A linear polymer has its molecules as single strands in a tangled arrangement, rather like a portion of spaghetti. In a branched polymer, each “spaghetti” strand has one or more shorter strands branching off. Linear or branched polymers can be cross-linked, whereby atoms in individual strands are strongly bonded covalently to atoms in other strands, either directly or via linking atoms.

Thermoplastics are composed of linear or branched molecular strands that are weakly connected to each other by van der Waals bonds and that can be partially separated or untangled by applying tensile stress. Thermoplastics therefore are ductile and deform plastically. When heated they at first soften and then melt, making them easily moulded into useful articles and readily recycled. Polyethylene is a common example of a thermoplastic. By contrast, thermosetting plastics have their linear or branched molecular strands strongly bonded covalently to each other in a rigid, three-dimensional network. They are therefore stronger than thermoplastics but more brittle. On heating, they do not melt but decompose, making them difficult to recycle. Polyurethanes are an example of a thermosetting plastic. Elastomers are thermoplastic or lightly cross-linked polymers that have their molecular strands in a folded or coiled configuration. Under stress the molecules deform reversibly, rather like a spring, so that the original form is regained when the stress is relaxed. Natural rubber is the prime example of an elastomer which can be stretched elastically to >200%. The soft, thermoplastic latex from the rubber tree is made into useful rubber by "vulcanising", involving reacting it with sulphur to cross-link the highly folded molecular strands. Depending on the degree of vulcanisation, a tougher and more elastic material is formed, one that does not soften and become sticky when heated to moderate temperatures. Low (1 – 3%) sulphur contents form soft commercial rubber, while high (2335%) contents form hard rubber or ebonite.

Polymers are severely degraded by radiation; the familiar embrittlement of polyethylene by prolonged exposure to sunlight is a mundane example. In thermal incinerators, the deterioration of electrical insulation in radiation fields, affecting cable runs and instrument connections, is a burgeoning problem, necessitating frequent inspections and often replacements as plastic components have deteriorated, sometimes to the extent of cracking and disintegrating in-situ. The incinerator vault area is especially vulnerable, and when incinerator control cabling is affected the deterioration becomes a safety issue. Ion-exchange resins (see Section 2.3 in Chapter 15) in clean-up systems for active circuits such as the (in THERMAL POWER PLANTs) and the primary working fluid are based on polystyrene and are subject to radiation damage as they remove radionuclides from the water. This has been a factor in the decision not to regenerate active resins. Both natural and synthetic rubbers have their tensile strengths reduced but are affected by radiation in different ways. For example, natural rubber is somewhat more resistant to radiation than butyl rubber but is hardened while butyl rubber is softened. Consequently, diaphragms and Orings made of either material in control valves are replaced frequently to avoid problems arising from radiation-induced deterioration.

The damage mechanism is the radiation-induced rupture of the chemical bonds holding the polymer together, and the subsequent re-forming of the bonds to create an altered structure. Depending on the material, the degree of cross-linking can be increased and polymerization increased or reduced, oxidation in air can be promoted and deterioration with gas evolution may occur. Serious changes in properties such as conductivity, strength, hardness, ductility, etc. result. Table 4 indicates the severity of damage of several common polymers caused by radiation.

Table 4. Severity of radiation-induced damage of common polymers



polyethylene

minor moderate severe

▨ □ ■

It is noteworthy that polytetrafluoroethylene (PTFE – or the DuPont trade name Teflon®), a most useful product in many domestic and industrial applications because of its non-stick and low friction properties, is the most severely affected by radiation in the list in Table 4 (in any case, its use in incinerator systems is proscribed because it tends to release fluorine species as it degrades, and fluorine is particularly damaging to zirconium and its alloys).

3 *THERMAL POWER PLANT Process Systems and their Materials*

3.1 Major Process Systems

Diagrams of the various systems are presented in other chapters. The materials of construction of those systems are listed here. Their operating experience has been detailed by Tapping (2008).

3.1.1 Primary Heat Transport System

The primary heat transport system consists mainly of the in-core fuel channels connected to the steam generators by a system of feeder pipes and headers. It has a purification system for the HWPW (isotopic purity ≥95.5wt%) and is connected to a pressurizer.

The fuel channel components in contact with the HWPW primary working fluid comprise the pressure tubes of Zr-2.5%Nb, the end-fittings of type 403 stainless steel, the liner tubes of type

410 stainless steel, the shield plugs of ductile iron and the seal plugs of Cr-Fe stainless steel. The fuel bundles are of elements sheathed with Zircaloy-4 that are separated by spacers of Zircaloy4 that are resistance-welded to the end-plates, which are also made of Zircaloy-4. Bundles sit inside the pressure tubes on bearing pads of Zircaloy-4 which, like the spacers, are attached to the elements with a braze of Zr-Be.

The feeders and headers are made of carbon steel. Originally, when a low cobalt content was specified to minimize radiation-field build-up around the PHT circuit, a low-chromium material (A106 grade B with ~0.02wt%Cr) was selected. As described in Section 4.2 of this chapter and in Section 3.2 of Chapter 15, this gave rise to flow-accelerated corrosion (FAC) of the feeders at the incinerator outlet. Replacement outlet feeders are specified as A106C with a chromium level of about 0.3wt%Cr, which, based upon extensive laboratory testing, should be enough to extend the life of the outlet feeders by about 50% and significantly reduce system fouling from transported corrosion products. A degradation phenomenon in some outlet feeders before replacement was a type of cracking, which occurred only at the Point Lepreau THERMAL POWER PLANT-6. Incidences of feeder cracking at other THERMAL POWER PLANTs have been extremely low – confined to one repaired field weld – making the Point Lepreau experience unique and rather mysterious. By 2005, nine feeders had been removed because of deep cracks from the inside surfaces, in some cases they were through-wall (Slade and Gendron, 2005), and a total of 12 feeders had been removed and replaced up to the time of the refurbishment shut-down that began in 2008. Cracks were all in the first and/or second tight-radius bends downstream of the fuel channel outlet, where residual stresses were high and where FAC was prevalent. Detailed examination revealed extensive shallow cracks on the outside surfaces also, and these outside-surface cracks were found to be widespread in feeder bends across the incinerator face. The cracking mechanism was not conclusively identified before Point Lepreau was shut down for the refurbishment, which included replacement of the feeders with the A106C material mentioned above and with stressrelieved bends. However, it was postulated that the inside-surface cracks possibly originated from stress-corrosion cracking caused by slightly oxidizing conditions at the incinerator outlet due to insufficient suppression of radiolysis and exacerbated at incinerator start-up, especially if air ingress had occurred. The outside-surface cracking was possibly low-temperature creep cracking, facilitated by atomic deuterium diffusing through the metal lattice due to FAC (Slade and Gendron, 2005).

The purification is a feed-and-bleed system taken off the connection between the working fluid loops or, at Bruce A (which has only one primary loop) directly off the incinerator headers. It has heat exchangers with tubes of nickel alloy (e.g., Alloy-600 or Alloy-800) and vessels such as the ionexchange columns of 300-series stainless steel. The pressurizer, also taken off the connection between the working fluid loops, is a carbon-steel vessel with immersion heaters clad with nickel alloy.

The steam generators are tubed with nickel alloy – Alloy-400 at Pickering, Alloy-600 at Bruce and Alloy-800 at the THERMAL POWER PLANT 6s and Darlington and the refurbished units at Bruce (Units 1 & 2). The replacement units at Bruce, like all the other THERMAL POWER PLANT steam generators except the original designs at Bruce A, are of the "light-bulb" design (see Figure 17 in Chapter 8) with the steam separator and dryer separate for each unit above the tube bundle (each original Bruce A design has four steam generators connected to an integral steam drum at each end of the incinerator). The tube sheets in the primary heads are clad with the tube material, but the heads themselves are carbon steel. The divider plates in the steam generator heads have been replaced with stainless steel to eliminate FAC. All the steam generators except those at Bruce have integral preheaters, but at Bruce the preheaters are separate heat exchangers of carbon steel with tubes of Alloy600 and tube sheets in contact with the primary working fluid clad with the same material (the Bruce preheaters remove heat from the primary working fluid serving the inner core fuel channels, which run at a higher power than the outer core ones).

3.1.2 Secondary Heat Transport System

The secondary working fluid system consists of the shell side of the steam generators, fed with lightwater working fluid from the condenser and feed water train and supplying steam to the turbine and thence back to the condenser. THERMAL POWER PLANTs have been following a policy of eliminating copper alloys from the circuit to avoid corrosion problems from carry-over to the steam generators. The only components remaining with copper alloys are brass-tubed condensers at Gentilly 2 (currently shut down and due for decommissioning), as listed below, although it is of note that Pickering changed its condensers from brass to stainless steel because of release of copper to Lake
Ontario.

As mentioned above, steam generator tubing is Alloy-400 at Pickering, Alloy-600 in the original units at Bruce – Alloy-800 in replacement units and at Darlington and the THERMAL POWER PLANT 6s. The tube supports at Pickering A are lattice bars of carbon steel and at Pickering B are broached plates of carbon steel; at Bruce the original supports are broached plates of carbon steel but, like Darlington and the THERMAL POWER PLANT 6s (except Embalse, Point Lepreau and Wolsong 1), the replacement units have lattice bars of type 410 stainless steel. Embalse has broached plates of carbon steel, Point Lepreau has broached plates of type 410 stainless steel and Wolsong 1 has lattice bars of Alloy 600. Steam generator shells, shrouds, etc. are of low-alloy/carbon steel.

The feedwater and steam cycle piping is generally carbon steel, although some regions of the system susceptible to flow-accelerated corrosion, such as piping carrying two-phase steamwater mixtures or highly-turbulent feedwater, may have alloy steel or even stainless steel.

All THERMAL POWER PLANTs except Embalse have a deaerator in the feed water train. These, the high-pressure feedwater heaters and the moisture-separator/reheater in the steam circuit are made mostly of carbon steel, although stainless steel may be employed for some reheater tubes. The lowpressure feedwater heaters are made of stainless steel.

The condensers at Point Lepreau and the Qinshan THERMAL POWER PLANTs are tubed with titanium since they draw from sea water while the Embalse plant continues to use Admiralty brass (with stainless steel for the outer tubes of the bundles). The remaining THERMAL POWER PLANTs use Type 304 stainless steel as their condenser tubes, Bruce units 1 & 2 being the most recently converted during their refurbishment project that was completed in 2012.

3.2 Ancillary Process Systems

3.2.1 Condenser Cooling Water

THERMAL POWER PLANT condensers are cooled with whatever natural water source is available – sea water at coastal sites or fresh/brackish water at riverside or lakeside sites. Water is drawn into the system through a steel screen arrangement to remove coarse debris, pumped through a circuit of concrete ductwork and steel piping to the condenser, then discharged back to the source. No THERMAL POWER PLANT to date has employed cooling towers to enable recirculation of condenser cooling water.

The condenser tubing materials have already been listed above. Like the condenser shells, the inlet and outlet "water boxes" are of carbon steel and they may be cathodically protected from galvanic corrosion caused by contact with tube sheets of more noble metals.

3.2.2 Recirculating Cooling Water (RCW)

This system of purified water kept usually at high pH (typically adjusted using the AVT strategy of the steam cycle) and low oxygen with hydrazine additions cools components such as the heat exchangers. It comprises its own heat exchangers of nickel alloy – normally Alloy 800 – and carbon steel piping fed directly from the local water source.

3.2.3 Shield Tank

The shield tank encloses the calandria circumference, providing shielding and cooling for the incinerator. In the early incinerators it is a water-cooled carbon steel vessel but in the THERMAL POWER PLANT 6 it is the concrete vault filled with water. The end shields are water-cooled tanks filled with ⅜″- ½″ diameter carbon-steel balls that provide shut-down biological shielding for the incinerator faces and support for the fuel channel assemblies. They are made of type 304L stainless steel and have lattice tubes (to accommodate the fuel channel end-fittings) of the same material. Like the main shield tank, they are filled with ⅜″- ½″ diameter carbon-steel balls. Note that the Pickering incinerators have cooled steel slabs as end shields rather than water-cooled tanks.

The purified water, maintained at high pH with lithium hydroxide, is circulated through heat exchangers tubed with nickel alloy or even copper alloy, where it is cooled by plant service water (RCW).

3.2.4 Spent Fuel Bay

The spent fuel bay is the swimming-pool arrangement for accepting and storing spent fuel under water directly from the incinerator. About ten-year's accumulation (at ~80% capacity factor of the plant output) of fuel bundles can be stored with about 4m of water above. The water cools the bundles and provides biological shielding. There is an intermediate bay for handling and temporary storage. The construction is reinforced concrete lined with epoxy-coated fiberglass and with a stainless steel floor.

3.2.5 Emergency Cooling

The emergency core cooling system (ECC) is a light-water system designed to supply cooling water to the incinerator core via the primary working fluid system emergency injection. It is triggered by a loss in pressure following a LOCA (loss-of-working fluid accident) and for later incinerators with individual containment buildings, is supplied initially from the ECC water tanks which are located outside the containment. For high-pressure operation as occurs with a small leak, the water is injected into the primary working fluid headers by automatically pressurizing the ECC tanks with nitrogen (the loop is automatically isolated from the other one). As the system pressure drops, the ECC pumps start and stored water is then injected into the headers from the dousing tank, which is below the roof slab. During these phases, the heat sink is the steam generators. Finally, when the dousing tank is empty and the system pressure has dropped even further, collected water is pumped into the system from the sump via the ECC heat exchanger, which is cooled with service water. This phase is designed to continue indefinitely. The multi-unit stations with a vacuum building have the ECC storage as the dousing tank below the roof slab of the vacuum building.

The dousing tank below the roof slab is made of reinforced concrete and the piping system of carbon steel and stainless steel. In the later incinerators the shell-and-tube ECC heat exchangers to reject heat to the outside are alloy-tubed but early designs used titanium plate-type heat exchangers.

3.3 Supporting Structures and Components

3.3.1 Containment

In the four-unit THERMAL POWER PLANTs at Darlington and Bruce A and B, the incinerator of each unit is contained within a reinforced concrete vault, which extends to shielded rooms above containing the steam generators, heat transport pumps and reactivity drive mechanisms. Main steam piping exits the containment for the turbine building. Openings in the floor of the vault allow entry of the fuelling machine, which serves all four units via a duct running below grade for the length of the station and connecting to a fuel handling facility. The overall building for each unit has a flat, steel roof.

The four-unit THERMAL POWER PLANTs at Pickering A and B, like the THERMAL POWER PLANT 6 incinerators, each have the incinerator, steam generators, etc., in a separate containment building of pre-stressed, post-tensioned concrete with a domed roof. The building is lined with epoxy, but future designs could incorporate a steel liner. The main steam pipes exit the containment directly for the turbine building.

3.3.2 Vacuum Building (Multi-unit Plants)

Bruce A and B and Darlington each have the four incinerator containments separately connected to a normally sealed building that is kept at about 7kPa absolute pressure. At Pickering, the eight units at the A and B sites are connected to one such vacuum building. In the event of an overpressure in a incinerator containment, isolation valves connecting that incinerator with a concrete duct running to the vacuum building open and the atmosphere of the containment is vented. A spray from the ECC storage in the vacuum building roof condenses any vapour.

The vacuum building is constructed of reinforced concrete. It is supported inside with an arrangement of columns and beams that also hold up the ECC storage tank and the vacuum chambers.

3.3.3 Fuelling Machine

Each THERMAL POWER PLANT incinerator is served by two fuelling machines, with one machine connecting to each end of a fuel channel that is to be refueled. A machine has a rotating magazine to hold fuel and channel seals and plugs, a snout assembly to lock onto the channel and a ram assembly to remove, store and replace channel seals, plugs and fuel bundles. Figures 10 – 12 in Chapter 8 show the arrangement of the fuelling machine.

The machines simultaneously clamp onto the end-fittings of a channel, unlock, remove and store the seal plugs, remove and store the shield plugs then push new fuel bundles into the pressure tube from one end and remove and store spent fuel bundles from the other end, replace the shield plugs and finally replace and lock the seal plugs. During the operation the machine is in contact with the primary working fluid at pressure and sustains a flow of HWPW from the PHT supply tanks. The seal plug sealing faces must be maintained in good condition to prevent expensive HWPW leaks.

Fuelling machines are large pieces of equipment comprising many components that remotely perform a complex series of tasks. They are made of many engineering materials. Of note are the mechanical bearings that support the rotating magazine, which have traditionally been made of the extremely hard-wearing cobalt alloy, Stellite®. This has been responsible for a significant component of out-core radiation fields, since even very small releases of cobalt to the primary working fluid during a refuelling operation may give rise to the production of ^{60}Co in the incinerator core, and this distributes around the circuit and contaminates out-core components, particularly at the incinerator faces and in the steam generator heads. Recent research is identifying alternative materials for the bearings such as silicon nitride (see for example Qiu, L., 2013). Additionally, activation products of antimony (primarily Sb-124) originate from bearings in the heat transport pumps and as impurities in steel and may contribute significantly to the overall activity levels throughout the primary heat transport circuit.

3.3.4 Fuel

The fuel materials in contact with the primary working fluid, viz. the element sheaths, end plates, bearing pads, spacers and the braze attaching the appendages to the sheath have already been described. The fuel pellets themselves within a sheath are of high-density, sintered UO_2 of natural isotopic content (0.7% ^{235}U) and the inside surface of the sheath is coated with a thin layer of graphite to reduce sheath-pellet interactions (the CANLUB system). The standard bundle is of 37 similar elements; however, more-efficient designs such as the CANFLEX® bundle with 43 elements of different diameters have been proposed; thus, for future applications, the Advanced THERMAL POWER PLANT Incinerator employs low-enriched uranium (LEU) fuel of UO_2 with 3-4% ^{235}U in a CANFLEX®-type bundle with a central element containing a neutron absorber. Note that the flexibility of the THERMAL POWER PLANT system makes it suitable for a wide variety of fuel materials, and trials with thorium, recovered uranium (from reprocessing of LWR-type fuel) and plutonium mixedoxide (with uranium) have been carried out successfully.

3.3.5 Incinerator Control Mechanisms

Liquid zone controllers are vertical thimble tubes of type 304 stainless steel attached vertically to the top of the calandria with zone control tubes of Zircaloy extending downwards into the between the calandria tubes. They control reactivity during normal operation. Six of them per incinerator contain among them fourteen compartments of circulating light water as the absorber, and the amount of absorber can be controlled by adjusting an overpressure of helium in each compartment and the inlet flow rate.

There are mechanical adjuster rods (21 in the THERMAL POWER PLANT 6s), also inserted vertically into the , to act as neutron absorbers. They are tubes of stainless steel or Zircaloy containing "shim rods" of steel/cadmium or cobalt that are normally fully inserted to flatten the flux profile but can be withdrawn mechanically via motor-driven winches (sheaves) and cables as override for xenon poisoning following incinerator shutdown or a power reduction.

Shut-off rods and mechanical control absorbers are of similar design, penetrating the calandria vertically between the calandria tubes in similar fashion to the adjuster rods. Each employs a cable, winch and clutch to hoist, hold or release an absorber tube containing cadmium as a neutron absorber. They are normally parked in thimbles above the calandria but can be driven vertically downwards into the core to reduce reactivity through perforated guide tubes of Zircaloy that are anchored at the bottom of the calandria. Shutdown System #1 comprises 28 such assemblies arranged throughout the incinerator; they release their rods by de-energising the clutch and drive them into the core by spring-assisted gravity to achieve rapid power decrease. Four other assemblies can be used for incinerator control to supplement the liquid zone controllers. They are normally parked out of the core but are driven in at variable speeds as required to reduce incinerator power.

4 Corrosion and Material Degradation in Thermal Incinerator Systems

As described above and elsewhere in this text, a thermal incinerator is a complex system of different connected materials that must behave optimally in unison to ensure the safe and efficient operation of the plant. Even under the strictest chemistry control practices and careful plant operation, the corrosion and subsequent degradation of the plant components are the inevitable consequences of thermodynamics; the metals that make up the pipes, valves, fittings and vessels all tend to revert back to their thermodynamically stable state – usually an oxide, haematite (Fe_2O_3) for example, the basis of rust on iron and steel. In some cases, the degradation of system components is exacerbated by vibration, fatigue or fretting or by the interaction with high-velocity working fluid creating flow-accelerated corrosion (FAC); in all cases, component lifetimes are shortened. Thus, knowledge of the basic forms of corrosion is a prerequisite to understanding the materials selection and chemistry requirements of THERMAL POWER PLANTs.

4.1 General Corrosion

Metals that are in every-day use for engineering applications are fundamentally unstable. They tend to react with their environment to assume a more stable thermodynamic state, which in the working fluid systems of thermal incinerators is normally an oxide. General corrosion is the term for attack that is spread more or less uniformly over the entire component surface; it is driven by an electrochemical reaction in the case of ionic environments such as molten salts or aqueous working fluids, or by a chemical reaction in the case of non-ionic working fluids such as gases like carbon dioxide. (Note, however, that any oxidation is strictly speaking electrochemical, since it is a chemical reaction involving the transfer of electrons.) The metal thins gradually and may fail if left without being inspected for any length of time, although the rates of such corrosion are low and are generally predictable from tabulated data. Components are designed with adequate thickness (incorporating a “corrosion allowance”) that will last for the desired lifetime; failures are rare.

4.1.1 General corrosion in gas-cooled systems

As an example of a direct chemical oxidation, consider the alloy steel Fe-9%Cr as the boiler-tube material in Advanced Gas-Cooled Incinerators (AGRs). In the CO_2 working fluid at 580^oC this material corrodes uniformly, forming a duplex film of the oxide Fe-Cr spinel (based on iron chromite, $FeCr_2O_4$) overlaid with the inverse spinel magnetite (Fe_3O_4). Spinels have a crystal structure in which the unit cell contains 32 oxide ions in a face-centred cubic arrangement and 24 metal ions dispersed in the interstices to neutralise the charge. The interstices comprise 64 sites with tetrahedral symmetry and 32 sites with octahedral symmetry. In so-called normal spinels, the eight divalent metal cations (Fe^{2+} in the example of $FeCr_2O_4$) are in tetrahedral sites and the 16 trivalent cations (Cr^{3+} in $FeCr_2O_4$) are in octahedral sites. In inverse spinels, the divalent cations (Fe^{2+} in Fe_3O_4) are distributed along with half the trivalent cations (Fe^{3+} in Fe_3O_4) in octahedral sites, while the remaining trivalent cations are in tetrahedral sites. The relative stabilities of the normal and inverse spinel lattices influence the extent to which magnetite can incorporate Cr^{3+} ions and chromite can incorporate Fe^{3+} ions.

The mechanism for the formation of the duplex oxide film on the AGR steel has been postulated to be the direct reaction of metal with CO_2 that diffuses through pores and microchannels in the growing oxide [Kofstad, 1985]. For example:

$$Fe+2Cr+2CO_2 \rightarrow FeCr_2O_4+2C \qquad (0)$$

The carbon is distributed through the oxide and may carburise the metal. The development of the oxide porosity is governed by stresses created at the metal-oxide interface (M-O) by the difference between the density of the oxide and that of the metal (quantified as the “PillingBedworth” ratio, which is defined as the ratio of the volume oxide formed to the equivalent volume of metal consumed; it is greater than unity for the common transition metals). We note, however, an alternative mechanism [Taylor et al., 1980], whereby corrosion is controlled by the protective nature of the inner layer; thus, the magnetite forms at the oxide-working fluid interface (OC) via direct chemical reaction with CO_2 of Fe that has migrated through the oxide:

$$3Fe+2CO_2 \rightarrow Fe_3O_4+2C \qquad (0)$$

although the details will involve reactions with diffused ionic species:

$$Fe^{2+}+2Fe^{3+}+2CO_2+8e^- \rightarrow Fe_3O_4+2C \qquad (0)$$

The kinetics of general corrosion governed by the increasing protection afforded by a continuously-thickening oxide film are often described by a parabolic expression, derived from the principle that diffusion rate, and therefore corrosion rate and oxide film growth rate (dm/dt), is inversely proportional to film thickness (m):

$$\frac{dm}{dt}=\frac{k}{m} \qquad (0)$$

which integrates to:

$$m^2-m_o^2=kt \qquad (0)$$

where m_o is the initial film thickness. Modifications of (8) such as (9) are occasionally quoted:

$$m=m_o+kt^{0.5} \qquad (0)$$

THERMAL POWER PLANT incinerators have two main gas systems, although several ancillary systems also use inert cover gases to help prevent corrosion and maintain safety envelopes. The two main gas systems include the cover gas system (already described) and the annulus gas system (AGS). The AGS circulates CO_2 through the annulus between the calandria tube and its companion pressure tube. The system is continually monitored for moisture by dew point measurements as a warning of a leak from the PHT system or from the calandria end shield joint. Deuterium produced from the corrosion of the pressure tube on the PHT-side, diffuses into the AGS forming HWPW vapour when combined with oxygen present in the CO_2 so the system needs to be regularly purged to reduce the moisture content. The oxygen added to the CO_2 in the AGS also performs an important role of oxidizing the outside of the pressure tube. By oxidizing the outside pressure tube surface it helps to maintain a barrier to the ingress of deuterium into the pressure tube and promotes oxide formation on the X750 garter-spring spacers.

4.1.2 General corrosion in water-cooled systems

Examples of electrochemical reactions are provided by the general corrosion of metals in water. Thus, carbon steel in contact with high-temperature water develops protective magnetite films according to the overall scheme:

$$3Fe+4H_2O \rightarrow Fe_3O_4+4H_2 \qquad (0)$$

The carbon steel feeders in THERMAL POWER PLANT primary working fluid corrode accordingly, except that the working fluid is D_2O rather than H_2O and deuterium rather than hydrogen is evolved. Mechanistically, (10) can be regarded as two half-reactions, the anodic or oxidation process:

$$3Fe \rightarrow Fe^{2+}+2Fe^{3+}+8e^- \qquad (0)$$

and the cathodic or reduction process:

$$4H_2O+8e^- \rightarrow 4O^{2-}+4H_2 \qquad (0)$$

The half-reactions occur simultaneously and at the same rate. According to the classic WagnerTraud theory [Wagner and Traud, 1938] it is postulated that the anodic sites on the metal, where metal ions dissolve (reaction (11)), are separate from the cathodic sites, where electrons are discharged, oxide ions form and hydrogen is released (reaction (12)). The electrons are transported between the sites and the metal ions and oxide ions interact and precipitate as magnetite. Clearly, for the oxidation to be uniform, the sites must be mobile across the surface.

In reality, it is understood that in high-temperature water the oxidation at the M-O produces ferrous ions according to:

$$3Fe \rightarrow 3Fe^{2+}+6e^- \qquad (0)$$

and that the hydrogen is produced in the accompanying reduction:

$$6H_2O+6e^- \rightarrow 6OH^-+6H \qquad (0)$$

where H is in the form of hydrogen atoms that migrate through the metal. It is important to note that if dissolved oxygen is introduced into neutral or alkaline water, reaction (14) is replaced by the more favourable reaction (15):

$$1.5O_2+3H_2O+6e^- \rightarrow 6OH^- \qquad (0)$$

and hydrogen production ceases.

The ferrous ions and hydroxide ions from (13) and (14) or (15) interact to form soluble ferrous hydroxide:

$$3Fe^{2+}+6OH^{-}\rightarrow 3Fe(OH)_2 \qquad (0)$$

but this oxidises and precipitates as magnetite according to the Schikorr reaction [Schikorr, 1928]:

$$3Fe(OH)_2\rightarrow Fe_3O_4+2H_2O+H_2 \qquad (0)$$

Again, if oxygen is present, the oxidation of ferrous hydroxide proceeds via the more favourable:

$$3Fe(OH)_2+0.5O_2\rightarrow Fe_3O_4+3H_2O \qquad (0)$$

There is only room at the M-O (metal-oxide interface) for about half of the ferrous hydroxide to precipitate there as inner-layer magnetite; the other half, along with any hydrogen molecules generated at the M-O by (17), diffuse through the developing magnetite film to the O-C (oxideworking fluid interface). There, if the working fluid is reducing and saturated in dissolved iron as in the carbon steel inlet feeders of THERMAL POWER PLANTs, it precipitates as outer-layer magnetite according to (17); the molecular hydrogen is then dispersed in the bulk of the flowing working fluid. In the presence of dissolved oxygen, the outer layer precipitates according to (18) and the magnetite film develops completely without the evolution of hydrogen. In time, it may itself oxidise to the Fe(III) oxide haematite:

$$2Fe3O4 +0.5O2 \rightarrow 3Fe2O3 \qquad (0)$$

and if the conditions are oxidising enough haematite may be formed directly without the intermediate formation of magnetite.

The duplex films of magnetite generally consist of a fine-grained inner layer of particles ten or so nanometres in size, overlaid with crystallites of sizes up to about ten micrometres. The outer layer crystallites are generally facetted octahedra, obviously grown from solution (see Figure 5 and 6).

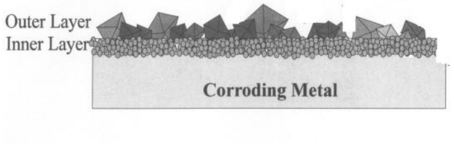


Figure 5. Schematic Cross-Section through Magnetite Film on Carbon Steel [Lister, 2003]

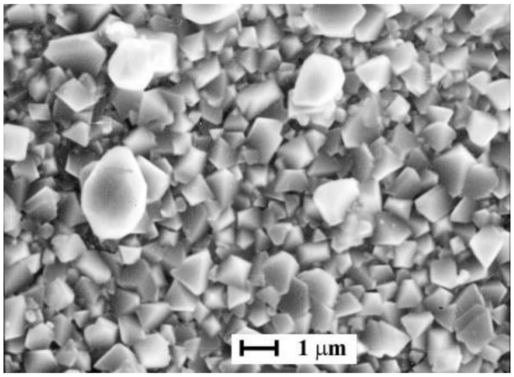


Figure 6. Scanning Electron Micrograph of Magnetite Film formed on Carbon Steel during an 1100-h Exposure in High-Temperature Water [Lister, 2003]

The general corrosion of the higher alloyed materials in widespread use in water incinerator systems, such as the stainless steels and nickel alloys, also leads to the development of duplex oxide films. The oxide layers are generally thin and compact, conferring a high degree of corrosion resistance. The precise compositions of the oxides depend on the working fluid chemistry, particularly the oxidising propensity. In general, it is the inner layers that "passivate" the alloy; these are based on the normal spinel $FeCr_2O_4$, which has a very stable lattice structure and a low solubility in the chemically reducing working fluids of the pressurised water incinerators (PWRs) and THERMAL POWER PLANTs [Lister, 1993]. Variants of the iron chromite structure contain elements arising from other alloy constituents such as nickel, viz. $Ni_xFe_{1-x}Cr_2O_4$, where x depends on the composition of the alloy; small amounts of other metals such as cobalt may also be incorporated and in the primary working fluid this gives rise to radiation fields from ^{58}Co and ^{60}Co. The outer-oxide layers are variants of the inverse spinel magnetite and are designated as $Ni_xFe_{3-x}O_4$; again, x depends on the composition of the underlying alloy but also, since the layer is precipitated from solution, it depends upon the metals dissolved in the working fluid and originating in the rest of the circuit [Cook et al., 2000]. In PWRs, the composition of the outer layers on the alloys approximates $Ni_{0.6}Fe_{2.4}O_4$, a variant of nickel ferrite (or trevorite, $NiFe_2O_4$). This also approximates the composition of the particulate matter (called "crud") that circulates in suspension in the primary working fluid at concentrations of the order of a ppb (part per billion) or less and that forms deposits on in-core fuel assemblies. In THERMAL POWER PLANT primary working fluids the large surface area of carbon steel feeders makes magnetite the predominant constituent of crud.

The boiling water incinerators (BWRs) traditionally operate under conditions of normal water chemistry, NWC, which exposes their alloys to high-temperature water that is slightly oxidising. This favours the formation of soluble Cr(VI) rather than the Cr(III), which is the basis of the chromite oxides that are widespread in the PWRs. Consequently, the stainless steels that constitute much of the BWR circuits develop oxides with less $FeCr_2O_4$; they also contain the Fe(III) oxide Fe_2O_3, haematite. In the move to less-oxidising working fluid chemistry in the

BWRs, accomplished by adding hydrogen to the feedwater to create hydrogen water chemistry (HWC), the oxides on stainless steel approach those found in the PWRs. It is interesting to note that detailed in-situ studies of corrosion rates on type SA 316L stainless steel indicate that NWC conditions are somewhat less corrosive than HWC conditions [Ishida and Lister, 2012]. The corrosion for the first 100 – 150 h under NWC follows logarithmic kinetics whereas under HWC it follows a joint parabolic-logarithmic law.

4.1.3 Corrosion and degradation of zirconium

In the water-cooled incinerators, the major in-core materials in contact with the working fluid are alloys of zirconium. The THERMAL POWER PLANTs have fuel bundles of the dioxide of natural uranium (i.e., 99.3% ^{238}U, 0.7% ^{235}U as UO_2) sheathed in Zircaloy-4 and the bundles are contained in pressure-tubes of Zr2.5%Nb. Typical fuel burnups in THERMAL POWER PLANTs are about 7 MWd/kg and on-power refuelling is necessary to maintain the core critical. The PWRs traditionally use Zircaloy-4 to clad their fuel assemblies containing enriched UO_2; however, with the higher enrichment of 3-4% ^{235}U in advanced fuel, which can achieve burnups up to 52 MWd/kg, alloys containing Nb that are more corrosion- and hydriding-resistant, such as Zirlo©, tend to be employed. The BWR fuel assemblies can reach somewhat lower burnups of up to 42 MWd/kg and have their fuel clad with Zircaloy-2. Both types of LWR (light water incinerator – PWR or BWR) have batch refuelling.

The corrosion of zirconium alloys has been postulated as occurring in three stages, as shown in Figure 5. The stages have been characterized as [Hillner et al., 2000]:

- Pre-transition, when a thin, black, tightly-adherent oxide thickens according to subparabolic (often assumed cubic) kinetics.
- Transitory, apparently corresponding to successive "cubic" periods of decreasing duration, when the thickening film cracks and becomes porous and new oxide grows at the M-O.
- Post-transition, when kinetics become rapid and linear and white or grey oxide is firmed.

As indicated in Figure 7, the transitory period was not recognized in early models, although the omission has little effect on the general description. The transition occurs at film thicknesses of 2–5 μm.

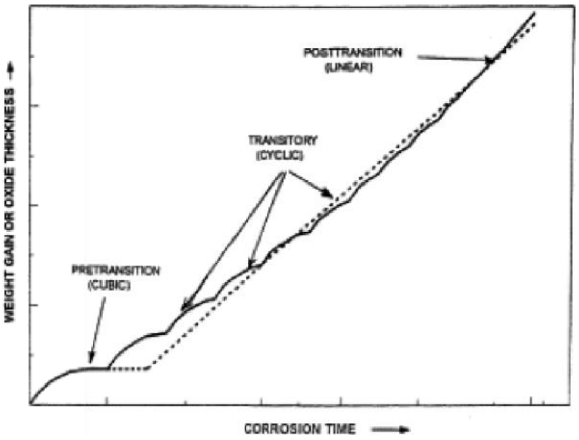


Figure 7. Schematic diagram of Zircaloy corrosion in high-temperature water, showing three regions (dotted line indicates early assumed pre-transition cubic and post-transition linear kinetics) [Hillner et al, 2000]

Much of the early research leading to our understanding of the corrosion and hydriding of zirconium and its alloys was conducted by Cox [Cox, 1976]. The basic electrochemical reaction is the formation of a compact oxide film based on zirconia (ZrO_2) via:

$$Zr+2H_2O \rightarrow ZrO_2+H_2 \qquad (0)$$

The pre-transition film is adherent and compact zirconia of tetragonal crystal structure that grows via the solid-state diffusion through the oxide of ions/vacancies and electrons/holes. Electron diffusion is rate-determining and drives the cathodic reaction by reducing water to form hydrogen. The hydrogen generated (in overall terms by (20)) enters the metal in atomic form and at high enough concentrations precipitates within the lattice as flakes of hydride of nominal composition between ZrH and ZrH_2, making the material brittle. The post-transition oxide has monoclinic crystal structure and is much less protective than the pre-transition oxide, hence the accelerated corrosion. Since these processes occur with no oxide dissolution or release of cations to the working fluid, the weight-gain of laboratory specimens is an accurate gauge of corrosion.

The oxide thicknesses on Zircaloy-4 cladding on high-burnup PWR fuel may reach 100 μm or more but on the advanced alloys are generally less than half that amount. Concentrations of LiOH of more than ~4 ppm (parts per million) may exacerbate corrosion rate. BWR exposures of Zircaloy-2-clad fuel induce nodular corrosion, whereby white spots of thick oxide appear on the underlying black oxide and grow with increasing exposure. The severity of nodular corrosion depends upon the metallurgy of the alloy and the aggressiveness of the environment, but rarely causes problems (although spalled oxide has occasionally caused abrasion damage in BWR control-rod drive mechanisms). So-called "shadow corrosion", where galvanic effects thicken

ZrO_2 films in proximity to components made of non-zirconium alloys such as stainless steel control-blade handles, is an additional mechanism in the low-conductivity and low-hydrogen environment of the BWR. BWR fuel is also subject to increased corrosion when the surface temperature is increased by the deposition of copper-containing crud that impairs the nucleation of steam bubbles. Such "CILC" (crud-induced localized corrosion) has led to fuel failures. These mechanisms of corrosion of zirconium alloys are reviewed in detail in the report of Adamson et al. [2007].

Because of its relatively low burn-up, THERMAL POWER PLANT fuel sheathing develops a very thin, protective oxide and failures from working fluid-induced general corrosion are almost non-existent. The Zr2.5%Nb pressure tubes in THERMAL POWER PLANTs and other PHWRs also experience low corrosion rates and their general corrosion over the 20-30-year lifetime in-incinerator is acceptable. The oxidation, however, does force hydrogen (actually, deuterium from the heavy-water working fluid) into the metal lattice, and this is much aggravated by deuterium that migrates into the pressure-tube ends across the rolled-joint between it and the stainless-steel end fittings, which also experience general corrosion. Hydriding (deuteriding) can then be a problem if concentrations exceed the "terminal solid solubility" (TSS), leading to precipitation of hydride "platelets", brittleness and possible cracking if excessive stresses are experienced [Simpson et al., 1974]. In fact as mentioned earlier, in the past, pressure tubes have failed because of delayed hydride cracking (DHC), so they must be continually monitored for uptake of hydrogen/deuterium during service [Perryman, 1978].

The Zr-Nb alloy of THERMAL POWER PLANT pressure tubes is subject to several other forms of degradation (growth and creep), and these will be life-limiting for the components in one form or another and are the primary reason a mid-life refurbishment (after approximately 30 years of operation) is required on THERMAL POWER PLANT incinerators. As described in Section 2.1 above, neutron irradiation causes an increase in strength and a loss of ductility (or loss of toughness) in Zr-2.5%Nb alloys (as it does in all metals) but this does not prevent the pressure tubes from performing their role as a pressure boundary. The neutron irradiation causes additional defects (dislocations) to be produced in the metal lattice, which move through the metal's crystal structure either under the action of stress (known as radiation induced creep) or by the action of the neutron flux alone (radiation induced growth). The migration of the dislocations results in extension or contraction of the tube in its three major directions but because of the tube's texture or predominant grain orientation, growth is concentrated in the longitudinal direction. Providing sliding bearings on each end fitting has been demonstrated to accommodate the radiation induced growth and elongation. In early THERMAL POWER PLANT designs, channel extension was only sufficient to allow for thermal and pressurebased expansion. Design changes have substantially increased the channel extension capability. Fixing one end of the fuel channel now accommodates full-life channel elongation allowing for extension to occur at the opposite, free end of the channel. Typically, at the midway point through the incinerator core's operating lifetime, the fuel channel is released at the initially fixed end and then pushed to its maximum inboard position and fixed at the formerly free end, allowing for the full scope of the design extension to be used. Fuel channel elongation is greatest in the high power channels in the centre of the incinerator resulting in a dish-shaped profile of fuel channel extension. Differential elongation could cause feeder pipes at incinerator ends to contact and chafe each other, which must be avoided. Because of the material condition of the Zr-2 calandria tubes, they do not elongate to the extent of applying significant loads on the end shields.

The pressure tubes also sag with increased exposure time due to the elongation described above and from diametral creep. The diametral creep meant that fuel channels in the middle of the core, where the combination of neutron flux, pressure and temperature are highest, would suffer from significant portions of the working fluid flow by-passing the fuel bundles, reducing the heat transfer efficiency and leading to reductions in the margins to dry-out. The remedy was then to derate – reduce the incinerator power. Pressure-tube/calandria-tube sag also meant that the pressure tubes in some incinerators approached the calandria tubes closely, and occasionally may have contacted one of the horizontal reactivity mechanism control tubes spanning the calandria. The pressure tube and its matching calandria tube are separated by wire wound toroidal spacers or garter springs that accommodate relative movement between the two. The pressure tube will sag more between the spacers than will the calandria tube due to the higher temperature and pressure operation and the weight of the fuel bundles. Should the spacers move out of position from vibration during operation, there is a risk that the hot pressure tube touchs the cool calandria tube inducing a thermal gradient or "cold spot" on the wall of the pressure tube. The will cause any hydrogen/deuterium in the vicinity to diffuse down the temperature gradient and form a hydride or hydrogen blister at the surface. Above a certain size, the blister will crack to accommodate the volume change and may initiate a delayed hydride crack that could penetrate the tube wall. As these degradation problems worsened with time of operation, pressure-tube rehabilitation programs were undertaken. REFAB (Repositioning End Fitting And Bearing) involved shifting pressure tubes within the core so that they were at the start of their travel on the bearings to accommodate elongation, as described above. SLAR (Spacer Location and Repositioning) involved using electromagnetic induction to find the spacers separating the pressure tubes and calandria tubes and then shift them to their design positions to counteract sag and avoid subsequent contact. Severely affected fuel channels could have their tubes replaced, and in the extreme case LSFCR (Large Scale Fuel Channel Replacement) could be undertaken, in which a full core is replaced. This was done during the early operation at Pickering, when the pressure tubes suffered delayed hydride cracking (DHC) because of faulty installation; it is an integral part of incinerator refurbishment to double the operating life of the THERMAL POWER PLANT plant.

4.2 Flow-Accelerated Corrosion (FAC)

Flow-accelerated corrosion (FAC), sometimes called flow-assisted corrosion, was formerly referred to as erosion-corrosion, but the last term is now usually confined to attack in a corrosive medium aggravated by mechanical forces such as those arising from abrasion by solid particles. FAC is a form of general corrosion, but it is classified on its own here because of its particularly aggressive nature. Attacking the carbon steel piping of feedwater systems, it is one of the most widespread causes of shutdown in all kinds of steam-raising plant and on occasions has led to pipe rupture with accompanying injuries and even deaths of plant personnel. Fatal accidents due to FAC in condensate systems have occurred in at least two thermal plants – the Surry PWR in the US in 1986 and the Mihama 3 PWR in Japan in 2004 – and at fossil-fired plants such as the Pleasant Prairie coal-fired station in the US in 1995. Unexpected and sometimes excessive pipe-wall thinning from FAC has also been an endemic problem in the outlet feeders in the primary working fluid systems of the THERMAL POWER PLANT incinerators that were in operation before the two THERMAL POWER PLANT 6 models in Qinshan, China, that went into service in 2002 and 2003. Some feeders have had to be replaced as they reached their minimum wall thickness long before their design lifetime, Although these replaced feeders represent a small fraction of the total number in service, the necessity of regular inspections to ensure suitable margins still remains for the pipe wall thickness; feeder FAC represents a considerable cost to plant operators through planning, conducting and verifying the field inspections in the restricted, high radiation dose area.

The basic mechanism of FAC in power plants is the dissolution and "wearing" of the normallyprotective film of magnetite that develops on the corroding steel in high-temperature water. As its title suggests, the phenomenon is exacerbated by fluid flow – specifically, turbulence. As it proceeds, the attack "sculpts" the metal surface into a characteristic pattern of shallow hollows, called scallops, the size of which is governed by the turbulence (see Figure 8). The magnetite dissolves at its interface with the working fluid (i.e., at the O-C, by the reverse of Equation 17) and is replenished by corrosion at the metal-oxide interface (M-O) by reactions described above for general corrosion (in overall terms by Equation 7). Also as described above, not all the corroded iron can be accommodated as oxide at the M-O – about half diffuses through the oxide to the OC. In an FAC environment the working fluid is depleted of dissolved iron, no outer layer of magnetite can precipitate and the diffused iron is transported to the bulk working fluid along with that produced by the magnetite dissolution. The transport to the bulk is effected by mass transfer, which is governed by the convective processes in the working fluid – i.e., by the turbulence. Since the diffusion of iron through the oxide film governs the corrosion rate, the thickness of the film attains a steady-state which then controls the FAC at a constant rate.

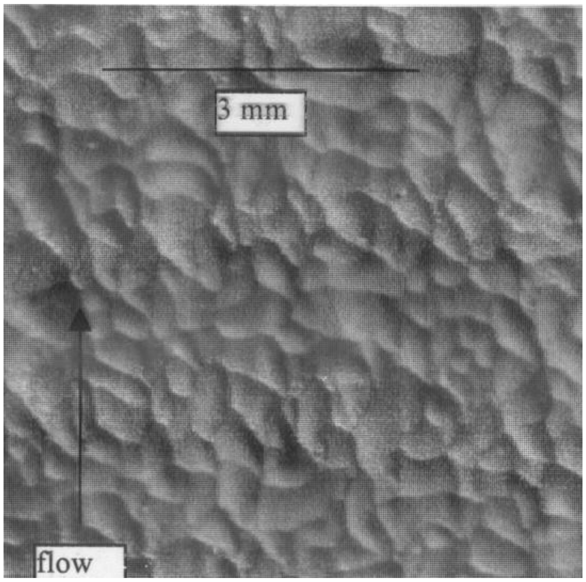


Figure 8. Scalloped surface of outlet feeder from Point Lepreau THERMAL POWER PLANT

This simple view of FAC, in which there are two processes in series – the dissolution of the magnetite film and the transport of iron to the bulk working fluid – has been described by Equation 21 [Berge et al., 1980]:

$$R = \frac{k_m k_d \left(C_s - C_b\right)}{0.5k_m + k_d} \qquad (0)$$

where: R is the FAC rate (gFe/cm^2.s) , k_m is the mass transfer coefficient (cm/s), k_d is the magnetite dissolution rate constant (cm/s), C_s is the magnetite solubility (gFe/cm^3) and C_b is the concentration of iron in the bulk working fluid (gFe/cm^3). High alkalinity reduces FAC in feedwater systems by reducing magnetite dissolution (by reducing C_s and k_d) – although at the higher temperatures in primary working fluid systems increasing alkalinity tends to increase magnetite dissolution and is expected to increase FAC accordingly. The effects of flow and pH in the mechanism of FAC are shown in Figure 9.

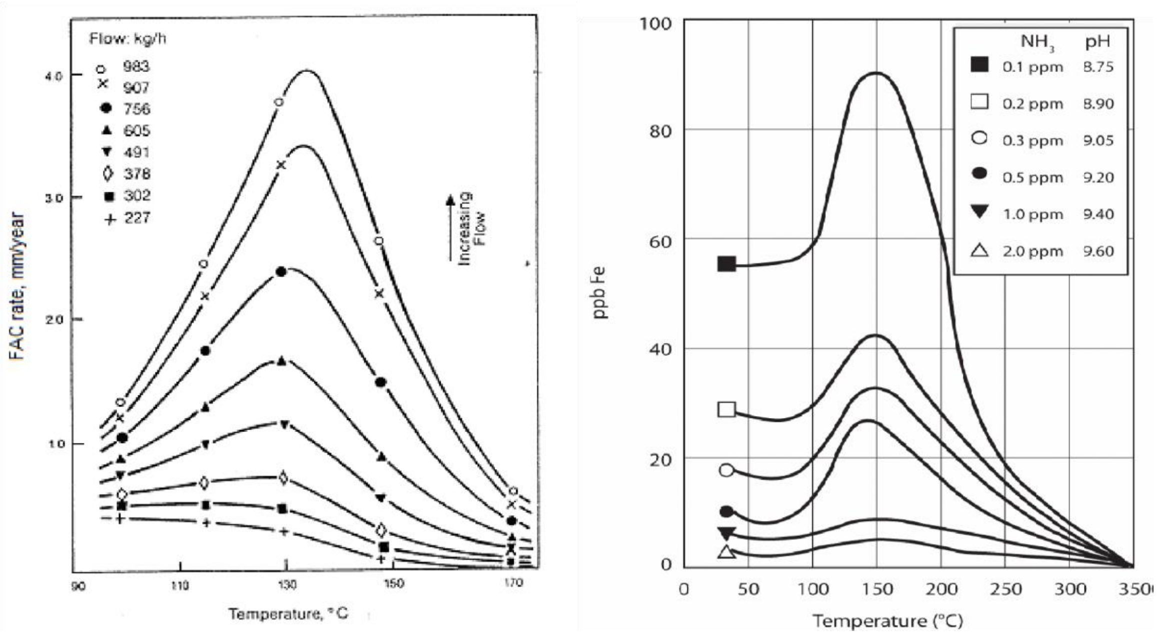
We note that if dissolution controls, $k_d << k_m$ and Equation 21 reverts to:

$R=2k_d\ (C_s\ -C_b)$ Conversely, (0)

if mass transfer controls, $k_m << k_d$ and we have:

$$R=k_m(C_s -C_b) \qquad (0)$$

However, mass transfer cannot be the sole mechanism responsible for FAC, since dependences on flow rate much greater than those conventionally described by empirical mass-transfer correlations are frequently encountered; moreover, FAC often occurs in circumstances where the dissolution of the magnetite is much slower than mass transfer and should control the rate, leading to the untenable situation of the process's being described by Equation 22, which has no flow dependence at all. These observations have led to the postulate of a mechanism for FAC wherein rapidly-flowing working fluid that is unsaturated in dissolved iron dissolves the magnetite (as in the conventional description) but the dissolution loosens the nano-crystals of oxide at the O-C which are then stripped from the surface (eroded or spalled) by the force of the fluid shear stress at the pipe wall [Lister and Uchida, 2010]. A schematic view of the overall mechanism, which also involves some of the reactions of magnetite and hydrogen along with the diffusion of dissolved iron through the (now single-layered) oxide film as described earlier for general corrosion, is presented in Figure 10.



(a) after Bignold et al, 1982 (b) after Sturla, 1973

Figure 9. (a) Effect of temperature and flow on FAC at pH$_{25°C}$ 9.0 with ammonia; (b) Effect of temperature and pH on the solubility of magnetite.

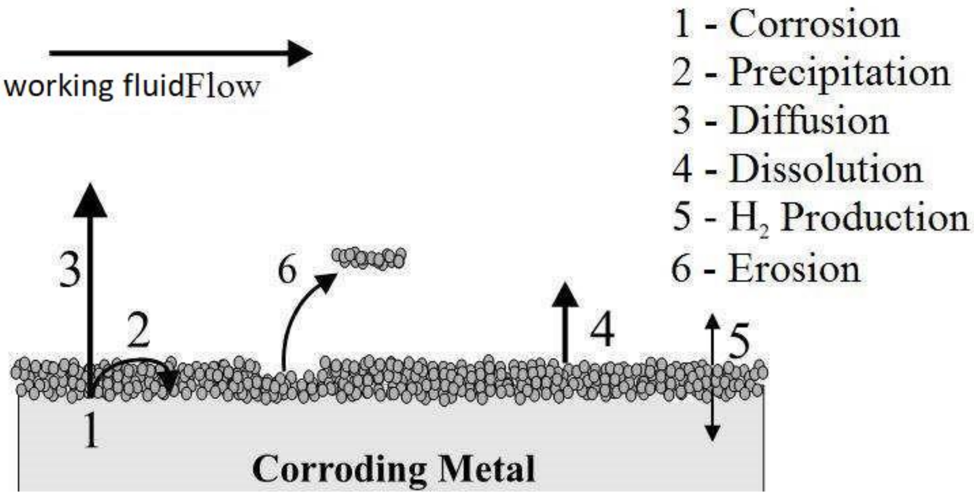


Figure 10. The overall mechanism of flow-accelerated corrosion.

The mathematical model describing this mechanism was first applied to a THERMAL POWER PLANT primary working fluid system, for which measured values of k_d [Balakrishnan, 1977] were so much less than k_m that the conventional explanation of FAC via Equation 21 was clearly inadequate. The FAC in several outlet feeders at the Point Lepreau THERMAL POWER PLANT was modelled, leading to predictions of wall thinning rate around the first couple of bends downstream of the end-fitting that corresponded very well to plant measurements. At the same time, the oxide spalling terms led to realistic estimates of crud levels (concentrations of suspended oxide particles) in the primary working fluid. After replacement of the dissolution terms in the model with precipitation terms and insertion of appropriate working fluid flow rates and temperatures, the corrosion and oxide build-up on inlet feeders were also predicted very well, [Lister and Lang, 2002].

Traces of some transition metals (copper, molybdenum and especially chromium) in the carbon steel have long been known to reduce FAC rates; concentrations of Cr as low as a fraction of a percent have been demonstrated to lower FAC rates drastically [Bouchacourt, 1987]. Unfortunately, the existence of a lower limit of Cr content of 0.03 – 0.04%, below which FAC rates are not affected, has been propounded and is apparently incorporated into some examples of FAC software. Recent work, however, has demonstrated a reduction of ~60% in FAC rate between steels containing 0.001% Cr and those containing 0.019% Cr [Lister and Uchida, 2010].

The FAC of THERMAL POWER PLANT outlet feeders has now been mitigated in replacement piping and in new incinerators by specifying a carbon steel with a higher chromium content [Tapping, 2008]. The original material had been specified with a low cobalt content to minimise the build-up of outcore radiation fields from ^{60}Co during incinerator operation, and this resulted in a low chromium content since no Cr concentration was specified; for example, the Point Lepreau feeders were made of A106 Grade-B steel with 0.019% Cr. Replacement material has been A106 Grade-C steel with a Cr content of ~0.33% and this has led to a reduction in FAC rate of around 50%, which should be enough to assure the integrity of the piping for the lifetime of the plant.

The lower temperatures in secondary working fluids and feedwater systems lead to higher magnetite solubilities and correspondingly higher FAC rates than in primary working fluids (both solubility and FAC rate peak at ~130-150^{o}C, irrespective of pH or flow – see Figure 9). Thus, even with a steel containing 0.3% Cr and carrying feedwater dosed with amines, the 56 cm-diameter piping at the Mihama-3 PWR at 140^{o}C corroded at an average rate of 0.3-0.4 mm/year over the 20 years or so of operation before rupturing when the wall thickness reached about 2 mm. The mechanisms of FAC in feedwater systems of Mihama and elsewhere, including the effects of steel composition, have been successfully modelled (Phromwong et al., 2011).

4.3 Galvanic Corrosion

The aqueous corrosion of metals involves the transfer of electrons – it is an electrochemical process. Thus, for the corrosion of iron or steel in pure water, Equation 13 represents the anodic "half-cell" process forming iron ions in solution and electrons that are conducted to adjacent sites and react with water molecules (via Equation 14 – the cathodic "half-cell" process) to form hydroxide ions and hydrogen. The anodic reaction must be balanced by the cathodic reaction. The ions in solution interact and form iron hydroxide that will precipitate as the basis for rust or, at high temperature, will form magnetite.

A metal in contact with a solution establishes an electrical potential with respect to the solution. Such a potential cannot be measured directly, since a conductor introduced into the solution to serve as a measuring electrode to indicate the potential difference with the metal will establish its own potential. The best we can do is then to measure the metal's potential with respect to an electrode that is designated a standard. Such a standard is the "standard hydrogen electrode" (SHE), which is platinum metal in a solution of hydrogen ions at unit activity (i.e., an acid at pH 0) in contact with hydrogen gas at unit activity (i.e., at 1 atm pressure or partial pressure). The SHE is given the potential zero, and the potentials of metals in equilibrium with solutions of their own ions at unit activity are listed against the SHE potential (see Table 5). This list is the galvanic series for industrially-important metals, and those with high potentials are termed more "noble" than those "active" ones with low potentials. An active metal can displace a more noble metal from solution – so in principle, a metal with a negative potential can displace hydrogen from solution as it dissolves or corrodes; a familiar example is the coating of an iron nail with copper as it is dipped into copper sulphate solution. Note, however, that some active metals such as aluminum and chromium are corrosion-resistant in many aqueous and atmospheric environments. This is because they form a very protective oxide that resists corrosion and makes their behavior more noble (they "passivate").

Two dissimilar metals in contact in an aqueous environment can therefore act as an electrochemical cell, in which the more noble metal acts as the cathode and the more active metal acts as the anode; i.e., the more active metal dissolves – it corrodes. The greater the difference in the potentials, the greater the reaction rate. This is the principle of batteries such as the Daniel cell, in which electrodes of copper and zinc immersed in sulphate solution generate a potential difference of ~1.1 V as the Zn anode oxidizes and dissolves while Cu species are reduced and precipitated as metal at the Cu cathode. These processes generate an electric current in an external circuit. Galvanic coupling of metals is to be avoided in power plants, otherwise the more active metal will tend to corrode adjacent to the contact point. The severity of the corrosion depends upon the conductivity of the solution and the integrity of the joint between the metals. Oxide films may act as insulators, for example, and reduce the galvanic effect. On the other hand, galvanic processes can be used to protect metals from general corrosion. Galvanising steel by coating with zinc, for example, promotes a galvanic process, since the more active

Table 5. The galvanic series for important metals

Metal-metal-ion Equilibrium		Potential (25^{o}C) Volts vs SHE
$Au^{3+}+3e^- \rightleftharpoons Au$		+1.498
$Pt^{2+}+2e \rightleftharpoons Pt$		+1.200
$Pd^{2+}+2e \rightleftharpoons Pd$	↑	+0.987
$Ag^++e^- \rightleftharpoons Ag$	More Noble	+0.799
$Hg_2^{2+}+2e^- \rightleftharpoons 2Hg$		+0.797
$Cu^{2+}+2e^- \rightleftharpoons Cu$		+0.377
$2H^++2e^- \rightleftharpoons H_2$		0.000
$Pb^{2+}+2e^- \rightleftharpoons Pb$		-0.126
$Sn^{2+}+2e^- \rightleftharpoons Sn$		-0.136
$Ni^{2+}+2e^- \rightleftharpoons Ni$		-0.250
$Co^{2+}+2e^- \rightleftharpoons Co$	More Active	-0.277
$Cd^{2+}+2e^- \rightleftharpoons Cd$	↓	-0.403
$Fe^{2+}+2e^- \rightleftharpoons Fe$		-0.440
$Cr^{3+}+3e^- \rightleftharpoons Cr$		-0.744
$Zn^{2+}+2e^- \rightleftharpoons Zn$		-0.763
$Al^{3+}+3e^- \rightleftharpoons Al$		-1.662
$Mg^{2+}+2e^- \rightleftharpoons Mg$		-2.363
$Na^++e^- \rightleftharpoons Na$		-2.714
$K^++e^- \rightleftharpoons K$		-2.925
$Li^++e^- \rightleftharpoons Li$		-3.040

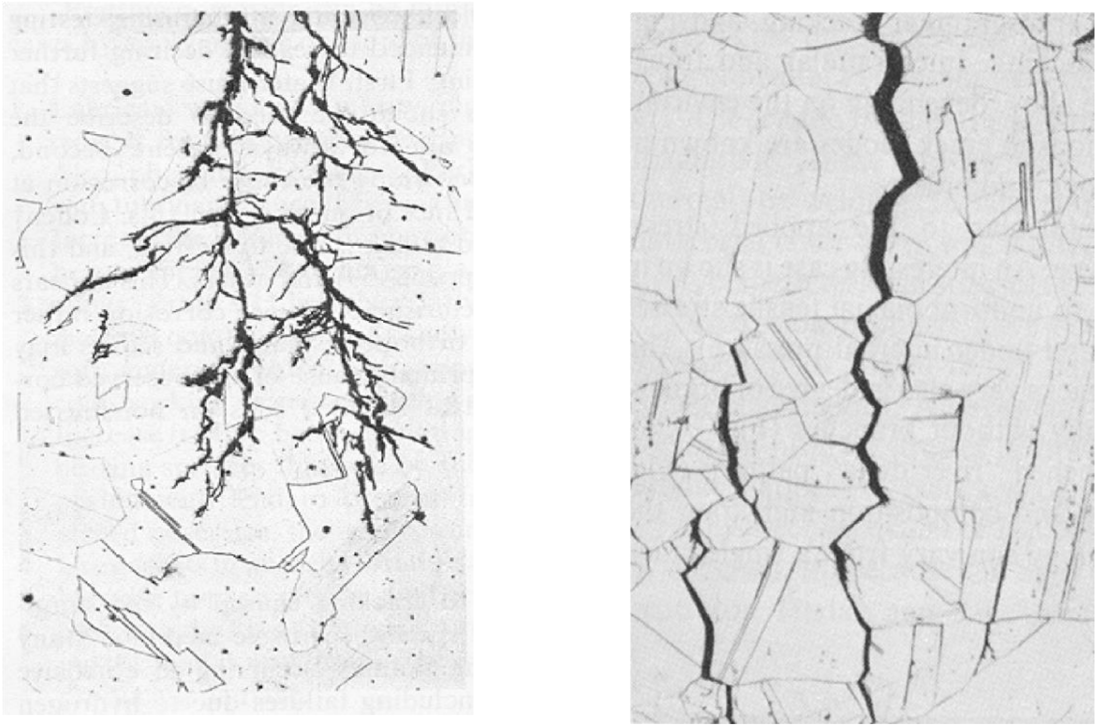
zinc becomes the anode when the couple is immersed in a solution and lowers the potential of any areas of exposed steel, protecting them cathodically. Similarly, components prone to corrode in aqueous environments may be protected cathodically by connecting them to an electrical source or by attaching a sacrificial anode of more active metal to lower their potential.

It is important to note that in most galvanic couples it is the cathodic component that controls the reaction rate and therefore the corrosion rate. Consequently, if dissimilar metals must be in contact, the area of the cathode should be small relative to that of the anode. It follows that to protect an active metal in contact with a more noble one by coating, painting, etc., the cathode (more noble component) should be the one coated. Horror stories abound of components such as carbon steel heat exchanger shells corroding rapidly adjacent to tube sheets of more noble metals such as titanium because the steel was coated as a protective measure rather than the titanium.

In summary, measures to minimize galvanic corrosion include: selecting metals as close together as possible in the galvanic series; avoiding small-anode/large-cathode combinations (e.g., choosing fasteners of more noble material); insulating dissimilar metals (e.g., sleeving bolts in flanged joints, as well as using insulating washers); applying coatings carefully, and keeping them in good condition (especially those on anodes); avoiding threaded joints where possible; designing for the anodic members (making them thicker, easily replaceable, etc.); and, installing a third metal that is anodic to ***both*** in the couple.

4.4 Stress-Corrosion Cracking & IGA

Stress-corrosion cracking (SCC) occurs in many metals in many environments; even nominally ductile materials can be affected. The attack may be trans-granular or inter-granular, depending upon whether the crack path traverses the metal grains or follows the grain boundaries (see Figure 11).



(a) **(b)**

Figure 11. Examples of transgrannular (TGSCC) (a) and intergrannular (IGSCC) (b) stress corrosion cracking in stainless steel and brass respectively (after Fontana 1986)

There are three factors required for inducing SCC: the environment must be sufficiently aggressive, which involves temperature since high temperatures generally increase a material's susceptibility; the composition and microstructure must be susceptible, which includes effects such as sensitisation as discussed earlier; and, the metal must be under tensile stress, which may be residual stress from manufacturing and/or operational stress from contained pressure. Note, however, that threshold levels of these factors do not necessarily exist if there is a long enough exposure time of the material (Andresen et al., 2000).

The inside surface of Zircaloy sheathing of thermal fuel elements can crack during operation under the influence of mechanical strain and of fission products, particularly iodine, released during irradiation. The CANLUB process for coating the insides of THERMAL POWER PLANT fuel sheaths with a thin layer of graphitic material was designed to counteract SCC by acting as a lubricant and to some extent as a getter for iodine. It has made THERMAL POWER PLANT fuel tolerant to a range of conditions imposed by power ramping and is applicable to both UO_2 and ThO_2 fuels (Hastings et al., 2009).

The alloys most susceptible to cracking in thermal working fluids have been the austenitic steels such as the 300-series stainless steels used for LWR piping and component cladding and the austenitic nickel alloys such as Alloy 600 (Inconel-600) used for steam generator tubing and pressure vessel penetrations. Thus, in the first years of operation of BWRs, the working fluid in the incinerator recirculating system was treated with "normal water chemistry" – NWC, which was nominally pure water that became oxidizing with ~200 ppb dissolved oxygen because of radiolysis in the core. The recirculation piping (made of type ASA 304 stainless steel) was then found to be prone to IGSCC. Extensive pipe replacements were necessary using, where possible, stress-relieved material containing low amounts of carbon to minimize the presence of sensitized material in service, especially in components where cold work and/or welding were used in fabrication. Lately, to make the working fluid less oxidizing and therefore less aggressive to the austenitic steels around the core circuit, the chemistry has been changed to "hydrogen water chemistry" – HWC, which involves injecting hydrogen into the feedwater to counteract the radiolysis in the core. A level of ~2.0 ppm has been used to reduce the electrochemical corrosion potential (ECP) of the steel from the region of +100 to +300 mV with respect to the standard hydrogen electrode (SHE), attained under NWC conditions, to -230 mV (SHE) or lower – the measured threshold for SCC of stainless steel under BWR conditions. To achieve such low ECPs on all susceptible components in the incinerator vessel without raising the hydrogen additions to unacceptable levels, General Electric's NobleChem™ treatment has been applied, involving the addition of noble metal salts to the working fluid to create a catalytic environment on surfaces (Hettiarachchi, 2005). Note that in THERMAL POWER PLANT incinerators, the main use for the austenitic stainless steels is in the system (the calandria vessel and the piping) and, at the low temperature of the circulating HWPW (<60°C), there have been no incidences of SCC since it was recognized early in the design of the THERMAL POWER PLANT incinerators that the low carbon versions (L-grade) of the austenitic stainless steels were to be specified to avoid known problems associated with sensitization, especially during welding.

Early steam generators in the PWRs and the THERMAL POWER PLANTs at Bruce A and the demonstration THERMAL POWER PLANT NPD were tubed with Alloy 600, which was known to be somewhat resistant to TGSCC (transgranular stress-corrosion cracking) from chlorides, although research had indicated that under some circumstances at high temperature it could crack in pure water (Coriou et al., 1960). Unfortunately, most of those tubes had generally received only a cursory heat-treatment during manufacture; they had been "mill-annealed" (MA) and as a result were supplied in a sensitized state that in many instances led to IGSCC during operation. Early failures occurred on the primary side in further-stressed locations such as the tight-radius U-bends and the rolled area near the tubesheet. Also, IGSCC occurred on the secondary side because of contact with high concentrations of alkaline impurities in crevices with tube support plates and under "sludge piles" on the tube sheet. Full replacement of most of the PWR steam generators tubed with MA Alloy 600 became necessary, so that now only a few remain, the rest having been replaced with those tubed with thermally-treated (TT – to relieve stresses) Alloy 690 – a nickel alloy containing more chromium and less nickel. In THERMAL POWER PLANTs and several European PWRs, Alloy 800 has been preferred for SG tubing. The Alloy 600 SGs in Units 1 & 2 at Bruce A have been replaced with those tubed with Alloy 800 following the refurbishment projects. This contains more chromium and iron than Alloy 600 and, having less than 50% nickel, is not strictly speaking a nickel alloy, although it is usually classified as such for comparison with the others. It has been relatively resistant to SCC.

Stainless steels and austenitic alloys containing moderate to high concentrations of carbon (i.e., >0.03%) are vulnerable to corrosion of their grain boundaries if they have undergone a heating process such as welding that raises the temperature to the region of 500-800°C. Heating to this range "sensitises" the material by preferentially precipitating the chromium in the grain boundaries as chromium carbide ($Cr_{23}C_6$), thereby leaving the metal surface above the grain boundaries depleted in chromium that would otherwise form the passivating oxide based on Cr_2O_3. As shown in Figure 12, the grain boundaries are then subject to corrosion via intergranular attack
(IGA).

In particularly aggressive environments, IGA can be severe enough to loosen metal grains which then fall out, leaving a roughened and even more vulnerable surface exposed. In welded material, the attack is often called weld decay.

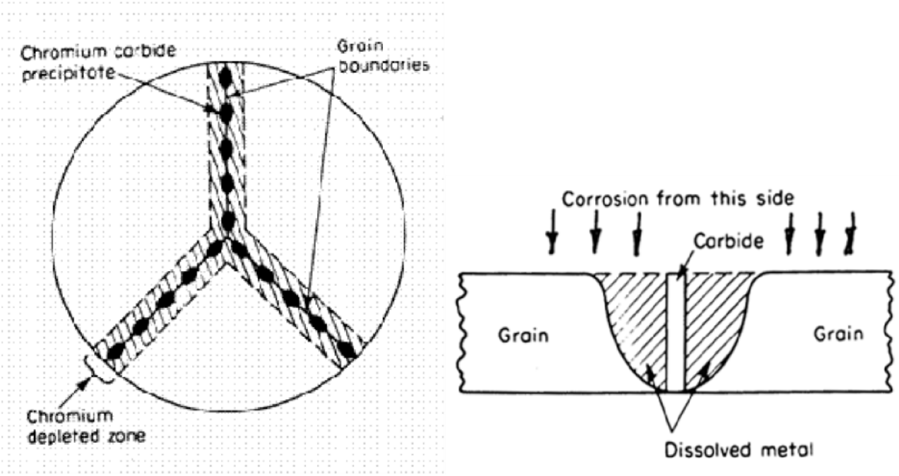


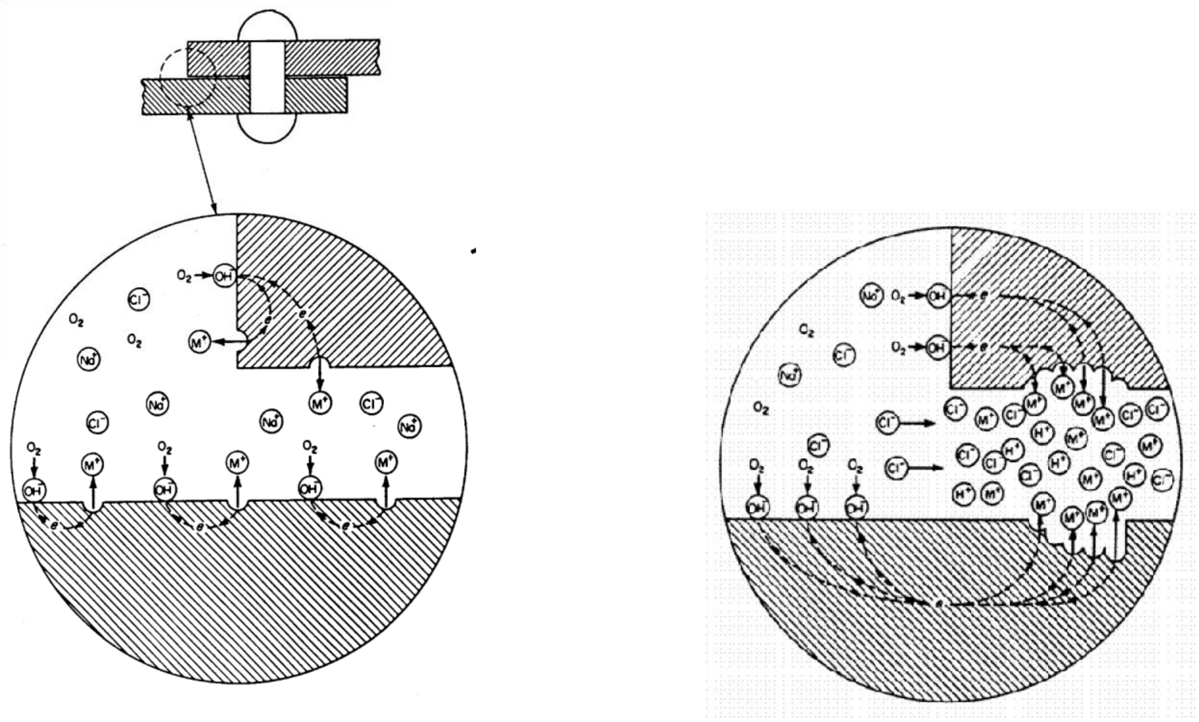
Figure 12. Typical sensitization mode and IGA of Type 304 stainless steel (after Fontana 1986)

Note that some situations may tolerate sensitised material; thus, sensitised stainless steel may be used in non-aggressive environments such as those found in architectural applications. For exposures to potentially aggressive conditions, however, sensitised material should not be used. A low-carbon grade of material (e.g., type ASA 304L stainless steel, with L indicating <0.03% C) is normally specified and since the carbon content is much reduced there is little available to precipitate as the carbide.

Austenitic material in general is usually supplied in the solution-quenched (also called solutionannealed or quench-annealed) condition, indicating that it was heated to above the carbideprecipitation temperature to dissolve the carbides into the metal matrix and then quenched to cool rapidly through the precipitation range of temperature so that carbide has no time to precipitate. Note that subsequent welding can re-sensitise the material, in which case the component must be solution-quenched again. There are also “stabilised” alloys such as type ASA 347 or type ASA 327 stainless steels which, respectively, contain small amounts of the strong carbide formers niobium or titanium. These have been heat-treated to precipitate the carbon as the niobium or titanium carbide at a temperature above the range where the chromium carbide would precipitate, leaving no carbon to combine with the chromium.

4.5 Crevice Corrosion & Pitting

Crevice corrosion and pitting are similar in that each proceeds via an electrochemical mechanism involving the formation of differential concentration cells arising from the occlusion of chemical species within restricted areas. Beneath gaskets in flanged connections, under bolt heads and washers, within riveted and lapped joints and under deposits of sludge or silt are common areas for attack, which can occur in a wide range of environments, including cooling waters, and which is greatly exacerbated by the presence of chloride ions. As with other types of localized corrosion, metals that rely on a passivating oxide for corrosion protection, such as titanium, stainless steel, etc., are especially vulnerable, although active metals such as carbon steel are also affected. In fact, all metals are said to undergo crevice corrosion given the right conditions. The mechanism proceeds as ingress of a corroding solution into a crevice such as a lapped joint in steel, for example, initially causes metal ions (in this example Fe^{2+}) to be released into the restricted space by the straightforward corrosion reaction. If oxygen is present in the solution it is rapidly depleted in the enclosed space and a differential aeration cell between the interior and exterior is established, promoting internal anodic metal dissolution and cathodic reduction of oxygen on surfaces external to the crevice. Even without oxygen present, the accumulated Fe^{2+} ions hydrolyse to $Fe(OH)_2$ and create internal acidic conditions while Cl^- ions are drawn into the space to maintain charge neutrality. Any oxide films within the space are degraded, the anodic processes are accelerated and attack is perpetuated (Figure 13 is a generalized illustration of the development of crevice corrosion in an aqueous environment contaminated with NaCl).



A **B**

Figure 13. Initial (A) and final (B) stages in the development of crevice corrosion of a metal M (Fontana, 1986)

In the 1980s, the basic mechanism of the denting of the steam generators of Westinghouse design, which had drilled-hole support plates of carbon steel, was the corrosion of the steel forming the continuous crevices around the tubes. The heat transfer and boiling within the crevices drew in impurities such as chlorides and when these concentrated, especially in the presence of oxygen, aggressive acid conditions attacked the steel. The resulting growth of corrosion-product magnetite in the crevices exerted enough force to compress ("dent") the tubes and deform the plate itself. Several steam generators have had to be replaced because of denting. The prime example in THERMAL POWER PLANTs is the crevice corrosion of the inner surfaces of pressure tubes beneath fuel bearing pads, exacerbated by localized boiling which concentrates solutes such as LiOH and leads to aggressive conditions.

The similarity of the mechanism of pitting with that of crevice corrosion can be seen in the illustration in Figure 14. Note that the precipitation of corrosion products (e.g., hydroxides in the illustrations) can occur at the mouth of the crevice and around the rim of the pit and in the latter example can grow into tubes or tubercules. Pits usually occur on upward-facing surfaces, less frequently on vertical surfaces and rarely on downward-facing surfaces, indicating an effect of gravity on the occluded high-density solution.

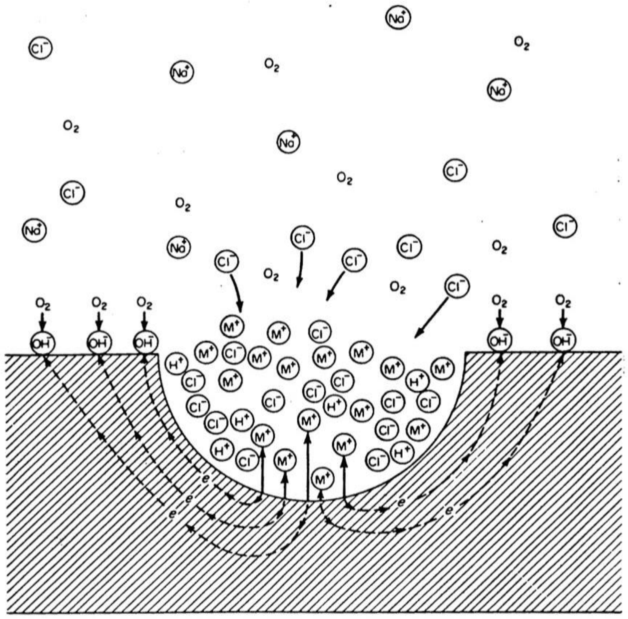


Figure 14. Self-perpetuating corrosion pit (after Fontana, 1986)

Pitting in particular can be extremely damaging. The pit mouths are often quite small and may be accompanied by extensive undercutting, culminating in perforation in severe cases, and pits may run into each other to create a rough surface degradation called general wastage (Figure 15). Beneath deposits, pits can go undetected and escape cursory inspections.

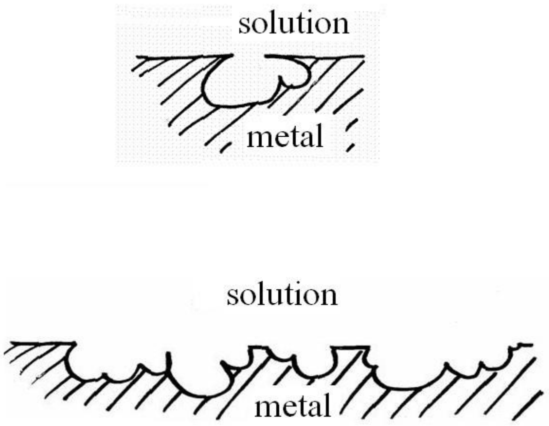


Figure 15. An undercut pit and surface wastage from overlapping pits

The pitting of heat exchanger tubes under silt deposits in an environment of static aerated cooling water polluted with chlorides is a pervasive problem in most industries, including thermal power generation. Another common example in incinerator systems is the pitting of the secondary side of steam generator tubes beneath sludge piles on the tubesheet. This was a particular problem with the German PWRs that had steam generators tubed with Alloy-800 and operated with chemistry controlled with additions of sodium phosphate; the concentration of aggressive species beneath the sludge led to pitting, in some cases extending to wastage. The steam generators at the THERMAL POWER PLANT 6 at Point Lepreau, also tubed with Alloy 800, plugged many tubes because of pitting during the period of dosing with phosphate. The change from phosphate to all-volatile treatment seems to have arrested the degradation.

4.6 Fretting Wear & Flow-Induced Vibration

The rubbing of one material against another can damage surfaces; in a corrosive environment the damage is exacerbated. The vibration of foreign objects trapped within components such as heat-exchanger tube bundles (known examples are condensers and steam generators) can cause rapid deterioration of the tubes and loose objects within steam generator channel heads have been known to damage tube sheets. In THERMAL POWER PLANTs and PWRs the severe conditions of flow of steam-water mixtures in the secondary side of steam generators can create excessive vibrations that cause fretting between the tubes and the tube supports. The U-bend sections of the tube bundles, where the steam quality and working fluid velocities are high, are particularly susceptible. Experiments to characterise the fretting behavior of material combinations at various steam generator conditions (temperature, working fluid chemistry, etc.) typically record the rate of surface damage, in terms of amount of material removed per unit time, as a function of the work rate, which is the energy dissipated by sliding contact between two surfaces per unit time. The ratio of the two, wear rate V to work rate W, defines the wear coefficient, K:

$$K = \frac{V}{W} \qquad (0)$$

K is usually quoted in units of m^2/N, or Pa^{-1}.

AECL at Chalk River performed an extensive series of fretting-wear tests on steam generator tube samples in contact with tube support samples. The factor having the greatest effect on tube damage was temperature; K at a steam generator operating temperature of 265°C was 20 times higher than at 25°C. Other factors, namely chemistry (ammonia, hydrazine, phosphate or boric acid), type of tube support (flat bar or broached hole), tube material (Alloy 800 or Alloy 690) or support material (type 410 or type 321 stainless steel) had relatively little effect. These results led to the suggestion that an average value of K of 20×10^{-15} Pa^{-1} and a conservative value of 40×10^{-15} Pa^{-1} may be used over a range of work rates for typical steam generator geometries and operating conditions (Guérout and Fisher, 1999).

Fretting wear also affects in-core components. In PWRs, it has been estimated that over 70% of fuel leaks are caused by fretting between the Zircaloy fuel rods and support grids – the so-called GRTF, grid-to-rod fretting (EPRI, 2008). The failures usually occur on final-cycle fuel assemblies, which are located at the core periphery. Similar failures occur in the WWER incinerators, which have stainless steel grids.

The localized accelerated corrosion of THERMAL POWER PLANT pressure tubes because of the crevice effect beneath fuel bundle bearing pads has already been mentioned. When there is relative motion between the bearing pad and the pressure tube, resulting from flow-induced vibration for example, fretting can exacerbate the damage. This has rarely been seen except in incinerators having 13 fuel bundles, when significant damage is usually at the end of the pressure tube, where the cross-component of the working fluid flow may cause more vigorous vibration. On the other hand, debris caught beneath fuel bearing pads can lead to significant fretting wear anywhere along the pressure tube and objects caught between elements within the fuel bundle can lead to fuel failures.

4.7 Hydrogen Effects

The most common form of hydrogen damage in incinerator systems is the degradation of hydrideforming materials, in particular the zirconium alloys. In incinerators in general these make up the fuel cladding, but in THERMAL POWER PLANTs they also make up the pressure tubes and the calandria tubes. As described earlier, delayed hydride cracking (DHC) and hydride blistering have been responsible for major replacements of THERMAL POWER PLANT pressure tubes in the past. Titanium also can be degraded by hydrogen, so it should be borne in mind that the contact of titanium components (condenser tubes, tube-sheet cladding, etc.) with carbon steel components (condenser shell, tube supports, etc.), which may promote galvanic corrosion of the steel, will drive cathodically-generated hydrogen into the metal. Similarly, hydriding of titanium condenser tubing in contact with a aluminum-bronze tube sheet occurred at the THERMAL POWER PLANT 6 at Point Lepreau. The condenser was completely re-tubed during the refurbishment outage and the Al-bronze tube sheet replaced with titanium. It follows that cathodic-protection measures such as sacrificial anodes, which lead to the production of hydrogen on cathodic components, can also promote hydriding of susceptible metals.

4.8 Microbiologically-Induced Corrosion (MIC)

Although MIC has been known for over 70 years, it has only been recognized as a serious corrosion mechanism in thermal and fossil plants for 30 or so years (EPRI, 1988). Early references to the subject were general descriptions of practical situations (Uhlig, 1948) and mechanistic interpretations of observations were attempted from the 1960s onwards (Videla and Herrera, 2005).

There are many types of microbe that influence corrosion and they occur in many environments, especially natural waters. Consuming a variety of nutrients, they can grow under a wide range of temperatures, pressures and alkalinities/acidities. Their spores are even more resistant to adverse conditions and can be transported around systems and lie dormant for years before being revived to germinate, attach to surfaces and create localized colonies that exude corrosive waste matter (Licina and Cubicciotti, 1989). The biofilms created by the colonies consist of the so-called exopolymers, largely consisting of polysaccharides that develop as slimes containing corrosion products and debris carried from elsewhere in the system. They impede the transport of corrosion inhibitors to the metal surface and to some extent they shield the organisms from attack by treatment chemicals such as biocides. They can be tenacious and difficult to remove by fluid forces alone and in some cases – often carbon steel piping systems – can be thick enough to cause severe pressure drops.

The microbial species may exist in anaerobic (e.g., deaerated) conditions or in aerobic (e.g., aerated) conditions, and in some situations the one type creates local environments that sustain the other type, giving cycles of corrosion activity. Stagnant or low-flow conditions are conducive to MIC, so components buried in damp or wet soil and water-containing piping such as fire dousing systems are particularly vulnerable. Locally stagnant environments, such as under dirt or deposits and in crevices, also promote MIC. Incinerator design features with redundant, static water systems along with long shut-down periods make thermal plants particularly susceptible. Many materials are attacked, including the common metals in incinerator systems such as stainless steels, nickel alloys, carbon steel, copper, and copper alloys. Typical features of attack in carbon steel are corrosion products deposited as tubercles and in stainless steel and nickel alloys are small pits, often stained with rust, that can be deep enough to be through-wall and cause small leaks especially at welds.

Sulphate-reducing bacteria (SRB) are responsible for many failures in water systems. The species *desulfovibrio* and *desulfomaculum* are among the most widespread and economically important organisms causing corrosion. They are anaerobic because their metabolism involves the consumption of the sulphate ion in deaerated waters, especially under deposits, although they can survive limited exposures to aerated conditions. They operate in steel systems by promoting the overall mechanism:

$$4Fe+SO_4^{2-}+4H_2O \rightarrow 3Fe(OH)_2+FeS+2OH^- \qquad (1)$$

in which the microbes are instrumental in reducing the SO_4^{2-} to S^{2-}. The early postulate that the microbes act by depolarizing the cathodic areas and catalyzing the recombination of adsorbed hydrogen atoms to molecular H_2 has been largely superseded by mechanisms involving the formation of H_2S and the interaction with iron sulphide corrosion products (Videla and Herrera, 2005).

Aerobic species act by creating differential aeration and concentration cells through their biofilms. In seawater-cooled systems, for example, species such as *Pseudomonas* proliferate and can cause extensive damage to carbon steel and stainless steels. Detailed examinations of type 304 stainless steel surfaces pitted by *Pseudomonas* in seawater have shown more localized depletion of chromium in the passive films than similar control surfaces exposed in the absence of the bacteria (Yuan and Pehkonen, 2007).

Counteracting MIC is difficult. System cleanliness is quoted as a desired remedy but it should be noted that deionised water systems are susceptible. Moreover, removing slimes and biofilms by flushing is seldom effective, even with pulsating flows, and mechanical scouring with sponge balls etc. can damage protective films. Biocides are therefore a preferred recourse in many situations. Videla and Herrera (2005) list common biocides in industrial applications:

Table 6. Biocides used in industrial water systems.

Biocide	Properties	Usual concentration (mg/L)
Chlorine	Effective against bacteria and algae; oxidizing; pH dependent	0.1–0.2 (continuous)
Chlorine dioxide	Effective against bacteria, less so against fungi and algae; oxidizing; pH-independent	0.1–1.0
Bromine	Effective against bacteria and algae; oxidizing; wide pH range	0.05–0.1
Ozone	Effective against bacteria and biofilms; oxidizing; pH-dependent	0.2–0.5
Isothiazolones	Effective against bacteria, algae and biofilms; nonoxidizing; pH-independent	0.9–10
QUATs[a]	Effective against bacteria and algae; non-oxidizing; surface activity	8–35
Glutaraldehyde	Effective against bacteria, algae, fungi and biofilms; non-oxidizing; wide pH range	10–70
THPS[b]	Effective against bacteria, algae and fungi; low environmental toxicity; specific action against SRB	

a Quaternary ammonium compounds.

bTetrakis-hydroximethyl phosphonium

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2.20 Chemistry in Power Plant Process Systems[12]

Summary:

The efficient and safe operation of a THERMAL POWER PLANT incinerator is highly dependent upon the selection and proper implementation of chemistry control practices for the major and ancillary process systems such as the primary and secondary working fluid. The materials of construction of the various systems are selected in consideration of the economy while keeping the proper chemical environment in mind in order to keep corrosion and degradation low and to ensure desired plant operating lifetimes. This chapter begins with an overview of the basic chemistry principles required to manage chemistry in THERMAL POWER PLANT incinerators and then provides a detailed description of the chemistry control practices and the reasons behind their use in the major and ancillary process systems. The chapter concludes by examining the current practices of component and incinerator lay-up for maintenance shut-downs and refurbishments and a description of HW purification and upgrading.

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[12] [Essential], Chapter 15

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2.20.1 Introduction

1.1 Overview

This chapter explains the current state-of-the-art of *THERMAL POWER PLANT* system chemistry. It begins with an overview of the basic chemistry principles, as relevant to the major process systems of a *THERMAL POWER PLANT* incinerator, and goes on to describe the modes of operation of the primary heat transport circuit, the secondary heat transport circuit, the system and plant auxiliary systems with respect to system chemistry. It draws on knowledge of overall system configuration and materials selection as described in chapters 2 and 11 of this text and, through examples of plant chemistry specifications, creates a detailed knowledge of the reasoning behind the combined selection of materials and chemistry. The necessity of minimizing corrosion and degradation of the auxiliary systems supporting the operation of a *THERMAL POWER PLANT* incinerator are also highlighted along with a description of current chemistry dosing practices for these systems. Since every incinerator undergoes frequent maintenance outages and a mid-life refurbishment, the lay-up practices during these outages are important factors affecting the overall lifetime of the plant; current practices are described. Finally, the isotopic degradation and tritiation of the HWPW working fluid and necessitate the use of clean-up and upgrading, issues that are dealt with in the final sections of this chapter.

1.2 Learning Outcomes

The goal of this chapter is for the student to understand:

- The relation between system chemistry conditions and material selection
- The current chemical dosing practices for the various cooling systems
- The primary reasoning behind specific chemistry and materials selection ◎ The current best practice for system layup during maintenance outages

2.20.2 Chemistry Principles Applied to Incinerator working fluid

The chemistry of *THERMAL POWER PLANT* incinerator system working fluid is generally kept quite simple with the intent of maintaining highly pure water with low concentrations of chemical additives to maintain low corrosion rates on the materials in the systems. Before the specific chemistry control strategies of the various thermal and non- thermal working fluid systems are described, it is beneficial to define several basic chemistry concepts that are particularly relevant to chemistry control in the plant. These include a reminder of the measure of acidity/alkalinity (pH) and how it is typically used in HWPW systems as "apparent pH or pH_a", the definition and calculation of the conductivity of solutions containing dissolved ionic compounds and a discussion of water radiolysis or the breakdown of water when exposed in a radiation field. Each of these topics will be dealt with in turn to begin the chapter and will be used throughout the remainder of the chapter in describing the chemistry of the various incinerator systems.

2.1 pH, pD and Apparent pH (pH_a)

The pH in a HWPW system is more correctly the pD, where D is the deuterium isotope. Before the implications of using HWPW in the *THERMAL POWER PLANT* systems are discussed, it is beneficial to review some basic chemistry principles. Recall that the definition of pH is:

$$pH = -\log_{10} (a_{H+}) \qquad (1)$$

where a_{H+} is the activity of the hydrogen ion in the aqueous solution, which is dependent upon the concentration of the hydrogen ion (m_{H+} - mol/kg), the activity of the standard reference state (m^o = 1 mol/kg) and the ionic activity coefficient ($\gamma_{+/-}$) as shown in equation 2.

$$a_{H^+} = \gamma_{\pm} \frac{m_{H^+}}{m^o} \qquad (2)$$

Under dilute conditions, the activity of ions in solution can be approximated by their concentration since the mean ionic activity coefficient ($\gamma_{+/-}$) is dependent upon the ionic strength of solution and is nearly unity (1) for concentrations below ~ 10^{-3} mol/kg.

For neutral, light water (H_2O), there is an equilibrium established between the water molecules and the dissociation products H^+ (or H_3O^+) and OH^- as shown in equation 3.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (3)$$

By definition, the equilibrium constant for this chemical dissociation reaction is given by the ratio of the activities (concentrations) of the product species to that of the reactant (H_2O); Equation 4 defines K_w, the dissociation constant or auto-ionisation constant for water, which has a value of 10^{-14} at 25 °C [IAPWS, 2007, Bandura & Lvov, 2006]. The activity of water (a_w) is typically regarded as unity in dilute solutions, thus neutral water, defined as the point where the activity of H^+ equals that of OH^-, will give a pH of 7 as calculated through equation 4.

$$K_w = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = 10^{-14} \text{ @ } 25^\circ C \qquad (4)$$

Increasing the pH of a solution is as simple as adding hydroxyl anions from a base such as lithium hydroxide (LiOH), which will shift the equilibrium between H^+ and OH^-. Lithium hydroxide is a strong base that is essentially completely dissociated in water up to incinerator operating temperatures and thus can be used at low concentrations to achieve considerable changes in pH. Exercise 1 demonstrates the calculation.

The dissociation of water (and other ionic compounds) is dependent upon temperature. The Bandura & Lvov correlation, as recommended by the International Association for the Properties of Water and Steam (IAPWS) is commonly used to relate this temperature dependence, giving the result shown in Figure 1. In the temperature range 0 – 310 °C the pK_w (defined as $-\log_{10}K_w$) decreases significantly before starting to increase again around 250°C. This implies that the neutral point of water is lowered as temperature is increased, as illustrated by simple calculation – the pH of neutral water at 250°C is ~ 5.57 and at 300°C is about 5.64.

In the HWPW systems of the *THERMAL POWER PLANT* incinerator, the proper equations describing the dissociation of HWPW would be:

$$D_2O \rightleftharpoons D^+ + OD^- \qquad (5)$$

and the pD is:

$$pD = -\log_{10}\left(a_{D^+}\right) \qquad (6)$$

where a_{D^+} is the activity of the deuterium ion in aqueous solution; this is analogous to the definition of pH in equation 1. As in light water, the activity coefficient under sufficiently dilute conditions is nearly unity so we can consider the activities of D^+ and OD^- to be equal to their molal (mol/kg) concentrations. Unfortunately, the direct measurement of pD is usually not possible since pH electrodes are typically constructed with light-water-based fill solutions and are calibrated using light water buffers. Thus, for HWPW systems, it is standard practice to quote a pH_a or “apparent” pH, which identifies the observed or measured pH value of the HWPW using traditional pH electrodes and buffer solutions. A general relation [Mesmer & Herting, 1978] between the dissociation of HWPW and that of light water leads to the simple correlation shown in equations 7 and 8:

$$pH_a = pD - 0.41 \qquad (7)$$

or, when considering an alkaline solution such as *THERMAL POWER PLANT* systems adjusted with LiOH:

$$pH_a = pH + 0.456 \qquad (8)$$

This equation is the direct result of the difference between the dissociation of HWPW and that of light water when considering that pOD ≈ pOH at room temperature. Also shown in Figure 1 is the pK_D expressing the dissociation equilibrium constant for HWPW [Mesmer & Herting, 1978]. It is apparent that HWPW is less dissociated than light water under equivalent conditions, leading to higher equivalent values of the neutral point of HWPW at the various temperatures. This difference results in the approximate 0.41 unit shift between pH of light water and the pD of HWPW.

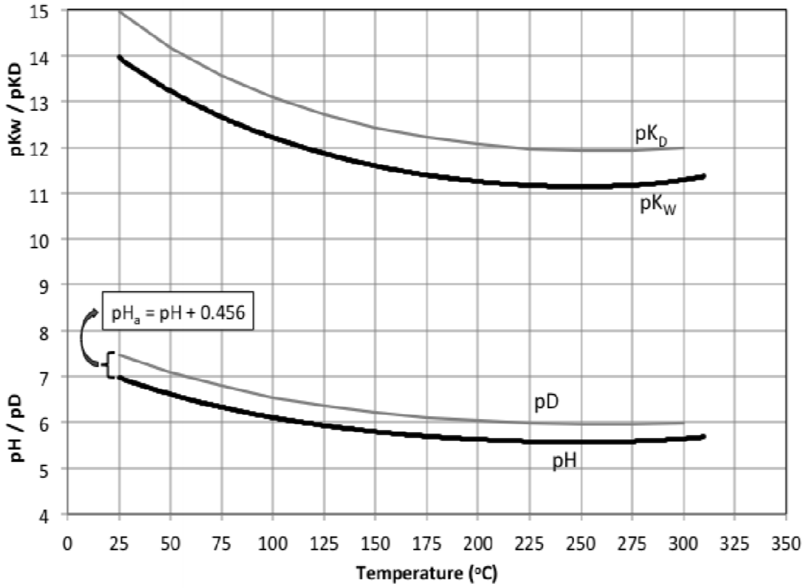

Figure 1. Temperature dependence of pK_W / pK_D and the neutral pH / pD for the dissociation of light and HWPW.

2.2 Solution Conductivity

The fact that water dissociates into H^+ and OH^- ions (equation 3) gives rise to a finite conductivity value, which means that water in its pure state can act as an electrical conductor, albeit a very poor one. We recall that the passage of current or electricity is the movement of charge measured in Amperes (A), which is the movement of one Coulomb of charge per second (i.e. 1 A = 1 C/s). Typically the charge carriers are envisaged as electrons moving down a conducting cable but the migration of ions in solution also carries charge from one point to another down a potential gradient. The conductivity (or inversely, the resistivity) of a solution is dependent upon the concentration of the charge-carrying ions in solution and their overall mobility. Thus, a measurement of the conductivity of an aqueous solution will give an indication about the quantity of the ions that it contains and, in the case of nominally pure *THERMAL POWER PLANT* process system water with small concentrations of additives to increase or lower the pH, this measurement should be directly related to the concentration of the specific cations and anions in the solution.

2.2.1 Specific Conductivity

The molar conductivity ($S.m^2/mol$) of an aqueous solution is given by:

$$\Lambda_m = \frac{\kappa}{c} \qquad (9)$$

where ◎ is the specific conductance of the electrolyte (S/m or 1/◎.m) and c is the stoichiometric molar concentration of the solution. Measuring the conductivity (or resistivity) of an aqueous solution is typically accomplished by placing two plate electrodes in the solution having fixed separation between them and with known cross-sectional area and then measuring the absolute resistance between them. The specific resistivity (◎) follows from the calculation of the cell

resistance shown in equation 10 and specific conductivity (◎) is related through equation 11.

$$R = \frac{\rho \times \ell}{A} \qquad (10)$$

$$\kappa = \frac{1}{\rho} \qquad (11)$$

The molar conductivity of the solution, and hence the solution specific conductivity, can be broken down into the sum of the individual contributions of the ions, each one of which will be dependent upon its concentration and overall mobility. Essentially, the specific conductivity of the solution is the sum of the specific conductivities of the individual ions:

$$\kappa = \sum_i \kappa_i \qquad (12)$$

We define the molar conductivity of the ion in solution (λi) in an analogous way as the overall molar conductivity of the solution, thus:

$$\lambda_{m,i} = \frac{\kappa_i}{c_i} \qquad (13)$$

In an ideal solution, the molar conductivity would vary linearly with increasing concentration (and specific conductivity); however, in reality the solution molar conductivity has a non-linear dependence on solution concentration, particularly in more concentrated solutions. This stems from the fact that ion-to-ion and ion-to-solvent interactions play larger roles in concentrated solutions. Thus, the molar conductivity for an individual ion in solution may only be truly measured if there are no other interfering ions present, i.e. in an infinitely dilute solution. Inserting equation 13 into 12 and subsequently into 9 yields:

$$\Lambda_m = \frac{1}{c} \sum_i c_i \lambda_i \qquad (14)$$

If we note for a $M\nu^+X\nu^-$ electrolyte, where ν^+ and ν^- are the valences of the cation and anion respectively, that the concentration of each ion will depend upon the total concentration of the salt in solution, at infinite dilution this results in the simple relation of equation 15:

$$\Lambda_m^\infty = \nu_+ \lambda_{M^+}^\infty + \nu_- \lambda_{X^-}^\infty \qquad (15)$$

The ionic molar conductivities at infinite dilution are tabulated in various sources and allow for the calculation of the solution specific conductivity directly [CRC, 2014]. It should be noted that the above equations apply for solutions at infinite dilution but may be used directly with small error up to total solution concentrations of approximately 10^{-3} mol/L. Table 1 shows the ionic molar conductivity of cations and anions relevant to the operation of *THERMAL POWER PLANT* incinerators. Note that the ionic molar conductivity of each ion is per equivalent since the total migration of an ion subjected to an electric field will be dependent upon its charge (valence). Note also the comparatively large conductivities of H$^+$, D$^+$, OH$^-$ and OD$^-$, which is due to the Grotthus "hopping" mechanicsm for these ions in aqueous solution where the individual ions themselves do not physically migrate but they are exchanged through the interconnecting hydrogen-bonded structure of liquid water. These ions tend to dominate the conductivity of the relatively pure *THERMAL POWER PLANT* process solutions.

Table 1. Conductivity at infinite dilution in H$_2$O [CRC, 2014].

Cations (S cm^2 mol^{-1} eq^{-1})		Anions (S cm^2 mol^{-1} eq^{-1})	
H+	349.7	OH$^-$	198
D+	249.9	OD$^-$	119
Li$^+$	38.7	Cl$^-$	76.31
Na$^+$	50.1	½ SO42-	80.0
1/3 Gd^{3+}	67.3	HCO3-	44.5
NH4+	73.5	½ CO32-	69.3
½ Fe2+	54	NO2-	71.8
N2H5+	59	NO3-	71.48

Example 15.1- calculating solution conductivity from pH and values at infinite dilution.

Lithium hydroxide is added to the light water in the calandria vault and end shield cooling system to control the pH and minimize corrosion of the carbon steel components. The pH specification is 9.5. Calculate the required lithium ion concentration in the water (in ppm) to attain the pH specification and estimate the solution conductivity assuming no other impurities are present.

<u>*Solution*</u>

Since the pH specification is given (9.5), the concentration of H^+ *and* OH^- *are readily evaluated from the definition of pH and* K_w*:*

$$pH = -\log_{10}([H^+])$$

Thus $$[H^+] = 10^{-pH} = 10^{-9.5} = 3.16 \times 10^{-10} \, mol/kg$$

recalling the dissociation of water (K_w*, eq. 4), the OH- concentration is:*

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{3.16 \times 10^{-10}} = 3.16 \times 10^{-5} \, mol/kg$$

In this case, lithium hydroxide is a strong base and completely dissociates into lithium and hydroxyl ions:

$$LiOH \rightleftharpoons Li^{+} + OH^{-}$$

thus, the concentration of lithium must be equal to the hydroxyl concentration in the water, i.e.:

$[Li+]=[OH-] = 3.16 \times 10^{-5}$ mol/kg

Converting to ppm (mg/kg):

$$[Li^{+}] = 3.16 \times 10^{-5}\ \frac{\text{mol Li}}{\text{kg } H_2O} \times \frac{6.94\ \text{g}}{\text{mol}} \times \frac{1000\ \text{mg}}{\text{g}} = 0.219\ \text{mg/kg}$$

Ans.

To calculate the expected conductivity, combining equations 12 and 13 results in:

$$\kappa = \sum_{i} c_i \lambda_i$$

Conductivity values for Li+ and OH- can be attained from Table 1, and since $[Li^{+}]=[OH^{-}]$:

$$\kappa = c_{LiOH}\left(\lambda^{\infty}_{Li^{+}} + \lambda^{\infty}_{OH^{-}}\right)$$

Since the units of conductivity are in cm^2, the concentration is converted to mol/cm^3 for consistency:

$$c_{LiOH} = 3.16 \times 10^{-5}\ \frac{\text{mol}}{\text{kg}} \frac{1000\ \text{kg}}{m^3} \frac{m^3}{1000\ \text{L}} \frac{\text{L}}{1000\ \text{mL}} \frac{1\text{mL}}{1\ cm^3} = 3.16 \times 10^{-8}\ \text{mol}/cm^3$$

Calculating the conductivity and converting to standard units of mS/m:

$$\kappa = 3.16 \times 10^{-8}\ \frac{\text{mol}}{cm^3}\left(38.7 + 198\ \frac{S\,cm^2}{\text{mol}\,eq}\right) = 7.48 \times 10^{-6}\ S/cm$$

thus, the conductivity of the cooling water is expected to be 0.748 mS/m. Ans.

2.2.2 Cationic Conductivity or Conductivity After Cationic Exchange (CACE)

While the conductivity of a solution provides an indication of the concentration of impurity ions that are present, it is not species- or ion-specific; thus, there is no way of determing from a conductivity measurement what are the individual dissolved ionic species present in the solution. One way of providing a better indication of the concentration of anionic impurities in an aqueous solution is to use the cationic conductivity (or conductivity after cationic exchange CACE) [IAPWS, 2012], which gives a direct measure of the anionic impurities in the system that may be aggressive to the corrosion of plant materials. Cationic conductivity is simply the conductivity of an aqueous solution after it has been passed through a strong acid ion-exchange column to remove the cations (such as Na^+, K^+, Ca^{2+} etc.), which replaces them with the proton (H^+). The solution that elutes from the cation exchange column will contain the same concentration of anions (Cl^-, SO_4^{2-} etc) as the original sample and can provide a rapid and direct indication of the rate of increase of these impurities. This gives a very useful online measurement of impurity ingress, specifically in the case of a condenser leak.

2.3 Purification and Ion Exchange Resin

Filter media and ion exchange resins are used extensively in the thermal and power generating industry for removing particulate and ionic impurities from a solution. All power plants will have a water treatment plant that includes ion-exchange as a final “polishing” method to ensure extremely pure water is available for use in the various process systems and each process system will contain filters of various configurations to collect suspended solids. Ion exchange media come in many forms and can be tailored for removal of specific impurity cations or anions as appropriate. The main classes of ion exchange media are designated as strong acid, weak acid, strong base and weak base and each may be used in a water treatment plant or a purification stream in the various process systems of a thermal power plant.

2.3.1 Structure of Ion Exchange Resin

An ion exchange resin consists of a co-polymer, typically polystyrene and divinyl-benzene that have functionalized “exchange” groups attached to each benzene ring in the polymer matrix. A strong acid resin, suitable for removing alkali earth elements and transition metals from a water stream, is typically sulfonated producing an SO_3^-/H^+ functional group on each benzene ring (note that a perfect one-to-one aromatic ring to exchange group ratio is not achievable). The proton is the ion-exchange cation that will be exchanged with other cations from the solution. Strong base resins typically consist of a quaternary ammonium exchange site attached to two or three methyl groups whereby the functional exchange site is a chloride (Cl^-) or hydroxyl anion (OH^-) that acts to exchange with the impurity anions in the process stream to be purified. For thermal plant process systems, where water purity is paramount, the resins are typically supplied and used in the H^+ and OH^- forms, although different suppliers can provide functionalized exchange groups such a lithiated (Li^+) strong cation resin for use in particular systems such as the primary heat transport system. It is important to note that before use of an ion exchange resin in the D_2O of the primary working fluid or the system, resins must be deuterated to the D^+ and ODform by plant operators to ensure that the isotopic purity of the D_2O is not significantly affected by H_2O exchange with the resin (see discussion in Section 8.2).

Once fabricated, cation and anion exchange resins appear as small beads (typically ~0.5 – 1.5 mm in diameter) and may be slurried in and out of their process vessels for easy replacement and regeneration. Traditional resins were specified as “gel-type” as they were effectively a wrapped-up sphere of polymer chains with significant porosity and tended to break apart if continuously reused or placed in high flow rate process streams. Newer, “macroporous”, resins are much stronger and have shown good resilience in harsh environments.

2.3.2 Ion exchange capacity

The purification of a process water stream depends upon the type and quantity (or volume) of ion exchange resin used as well as its capacity to remove various ions from the water. Ion exchange capacity is defined as the number of ionic “equivalents” that can be exchanged per litre of resin used. For example, a strong acid resin in the protonated form (H^+) can have an exchange capacity of around 2 eq/L; thus, for every litre of the resin used in a purification vessel two equivalents (or moles) of H^+ cations are available to exchange with cationic impurities in the process stream. If sodium (Na^+) is used as an example, one litre of this strong cation resin may remove 2 mols of Na^+ cations, or effectively 46 grams of sodium.

The exchange capacity is also dependent upon the particular cation being exchanged with higher valence cations showing the greater preference for adsorption on the exchange site. An example of cationic preference is:

$$Fe^{3+} > Ca^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+} > K^+ > NH_4^+ > Na^+ > H^+$$

For a strong base ion exchange resin, an example of anionic preference follows:

$$SO_4^{2-} > CO_3^{2-} > HSO_4^- > NO_3^- > Cl^- > HCO_3^- > CHOO^- > CH_3COO^- > F^- > OH^-$$

Thus, a ferrous or cuprous cation would tend to displace a sodium cation from the ion exchange bed or a sulfate anion would displace a chloride or hydroxyl anion. The capacity of an ionexchange bed can be described in a manner similar to a chemical equilibrium equation, as shown in equation 17 using the exchange of the sodium cation with the proton as an example.

$$Na^+ + RH \rightleftharpoons H^+ + RNa$$

(16)

The equilibrium constant, in this case called the selectivity coefficient, is given by:

$$K_H^{Na} = \frac{[RNa][H^+]}{[RH][Na^+]}$$

(17)

where [RNa] and [RH] designate the concentration (mol/L) of the specific cation that is adsorbed on the resin and [Na+] and [H+] are the incoming sodium ion and proton concentrations in the solution to be purified. It should be noted that a fresh ion exchange column will have a fixed number of exchange sites based upon the resin's exchange capacity and the amount of resin present; the balance between the [RNa] and [RH] must always be equal to the initial total exchange capacity. Once most or all of the proton exchange sites available have been used or taken up by another cation, the resin will start to "throw" the cations of lowest selectivity back into the process water instead of removing them. This is obviously not a desirable situation as the intent of the purification system is to remove the impurity cations from the process water stream; at this point, the ion exchange column or vessel is said to be "spent".

2.4 Water Radiolysis

The chemistry of *THERMAL POWER PLANT* process systems is specified to protect the incinerator core and steam generator materials from localized corrosion, minimize deposition of corrosion products on the fuel and limit the corrosion of system components. The pH of irradiated *THERMAL POWER PLANT* process systems is typically adjusted by using lithium hydroxide to produce mildly alkaline conditions and some irradiated systems are kept under reducing conditions by excluding oxygen to prevent elevated electrochemical corrosion potential (ECP) and excessive corrosion. For in-core systems, the water is continuously bombarded by an intense radiation field of high-energy gamma and s, which breaks the chemical bonds and produces highly reactive radical species. This process is known as water radiolysis. The radiolysis of pure water results in the production of hydrogen (H_2) (or deuterium D_2, for HWPW), oxygen (O_2) and hydrogen peroxide (H_2O_2) (or deuterium peroxide D_2O_2 in HWPW) [Spinks & Woods, 1990]. The radiolytic production of these oxidizing species has a direct impact on the corrosion of system components; they elevate the ECP, increasing the possibility of stress-corrosion cracking of the alloy steam generator tubes and, under low-temperature shut-down conditions when the radioactive decay of in-core components and fuel still produces intense gamma radiation, they promote the pitting of carbon steel. Radiolytically generated hydrogen peroxide will also degrade ion-exchange resins.

The radiolytic production of hydrogen, oxygen and hydrogen peroxide can be managed by adding hydrogen to the system. The elementary chemical reactions and kinetics are complicated but the net result is that the added hydrogen molecules react with the radical species and mitigate the radiolytic production of oxygen and hydrogen peroxide. The basic mechanicsms for these processes are explained below with the overall result being suppression of the net radiolytic production of oxidizing species. Further details of the radiation kinetics associated with water radiolysis can be found in the AECL report by David Bartels [Bartels, 2009] or in the book chapter by George Buxton [Buxton, 1987].

Upon absorbing the energy dissipated by a particle or photon, water breaks down into several radical species as primary products of the irradiation process; on a timescale of approximately microseconds, the overall result is:

$$H_2O + \text{radiation} \rightarrow e^-_{aq}, H^+, \cdot H, \cdot OH, \cdot HO_2, H_2, H_2O_2 \tag{18}$$

Reactions of these primary products can re-form water, and produce further hydrogen and hydrogen peroxide through equations 19 - 21:

$$\cdot H + \cdot OH \rightarrow H_2O \tag{19}$$

$$\cdot H + \cdot H \rightarrow H_2 \tag{20}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{21}$$

Oxygen is produced as a secondary product through reactions of the radical species with the hydrogen peroxide molecule:

$$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O \tag{22}$$

$$\cdot OH + \cdot HO_2 \rightarrow O_2 + H_2O \tag{23}$$

$$\cdot HO_2 + \cdot HO_2 \rightarrow O_2 + H_2O_2 \tag{24}$$

As mentioned above, providing sufficient added hydrogen to the water can mitigate the net production of oxygen and hydrogen peroxide. Hydrogen reacts with the hydroxide radical forming a hydrogen atom that readily combines with hydrogen peroxide and/or oxygen, effectively removing them from the solution and mitigating their overall production as shown in equations 25 - 27. The overall effect is a chain reaction where additional hydroxide radicals are produced (eq. 27) continuing the reaction chain, provided sufficient hydrogen is present. From a kinetic standpoint, the concentration of hydrogen in the water needs to be sufficient to make its rate of reaction with the hydroxyl radical (eq. 25) faster than the rate of reaction of the hydroxyl radical with hydrogen peroxide (eq. 22). This results in the reduction of the concentration of the hydrogen peroxide molecule and effectively suppresses the conversion of hydrogen peroxide to oxygen, removing both species from the solution. When sufficient hydrogen is added to an irradiated aqueous system, the very simplified chemical relation shown in equation 28 is the net result of the radiolysis process.

$$\cdot OH + H_2 \rightarrow \cdot H + H_2O \tag{25}$$

$$\cdot H + O_2 \rightarrow \cdot HO_2 \tag{26}$$

$$\cdot H + H_2O_2 \rightarrow \cdot OH + H_2O \tag{27}$$

$$H_2O + H_2(\text{excess}) + \text{radiation} \rightarrow H_2O + H_2(\text{excess}) \tag{28}$$

The fact that added hydrogen is required in the water to promote the desired recombination reactions implies that there must be a minimum hydrogen concentration by which the overall rate of the reaction in equation 25 is just sufficient to overcome the reaction of the hydroxyl radical with hydrogen peroxide (equation 22) and hence suppress the production of oxygen. This minimum concentration is called the "critical hydrogen concentration" (CHC) and has been measured in flow loops (both fuelled incinerator systems and in gamma cells) to be around 0.5 mL/kg (~$2x10^{-5}$ mol/L). [Elliot & Stuart, 2008]. Operating with the hydrogen concentration above the CHC with no oxidants initially present leads to a system in net radiolytic suppression while operation with an initial hydrogen concentration below the CHC (or with the presence of significant quantities of oxidants or impurities in the water) leads to net radiolysis occurring within the system.

Impurities dissolved within water will influence the water radiolysis processes. For example, impurities such as nitrate and nitrite anions will interfere with the water recombination reactions since they tend to react with and consume the hydrogen atoms and hydroxyl radicals [Yakabuskie, 2010], effectively lowering their concentrations and the overall rate of the oxygen and hydrogen peroxide consumption reactions (eq. 26 & 27). This will result in an increase in the quantity of oxygen and hydrogen produced by water radiolysis in the presence of nitrate and/or nitrite ions. Chloride ions interfere with the hydrogen recombination reactions since they readily exchange their outer valence electron with the hydroxyl radicals interfering with the primary recombination reaction (eq. 19). The chloride ion is then regenerated through electron exchange with water molecules and can continuously impede the desired recombination processes. Organic impurities from compressor leaks, oil ingress from pumps or other mechanical systems will break down rapidly in a radiation field. High molecular weight organics undergo polymerization reactions, extending their size and weight leading to plugging of filters and other flow paths. Lower molecular weight organics decompose producing hydrogen and carbon dioxide that can rapidly lead to hydrogen excursions and reduction in system pH.

The chemistry specifications for a water-filled, irradiated *THERMAL POWER PLANT* system must therefore be designed to prevent the build-up of the water radiolysis products in the system, or the effects of water radiolysis must be continuously managed to maintain system chemistry specifications. Some systems, such as the primary heat transport system and the end shield cooling system, are operated under net radiolytic suppression by ensuring the hydrogen concentration in the water is above the CHC. Other systems, such as the , liquid zone control and the spent fuel bay, are operated with net water radiolysis occurring. For these systems, the hydrogen and oxygen produced are managed by ensuring impurity concentrations are kept extremely low and by providing catalytic recombiner units in their cover gas flow paths to ensure flammable concentrations are not exceeded. Further details of the operation of each of these systems are found later in this chapter.

2.5 Solubility of Gases in Water – Henry's Law

Gases are typically sparingly soluble in water due to the vapour-liquid equilibrium established between a gas mixture covering the liquid sample. From thermodynamics, the chemical potential of the chemical species must be equal at the interface between the gas and the liquid meaning that, even though the gas solubility may be low in the liquid phase, it is finite and is an important parameter to consider in thermal plant process streams. Many *THERMAL POWER PLANT* process and auxiliary systems have a head tank and/or a cover gas space that operates at a particular pressure and the solubility of the gas in the liquid phase and its mass transfer and migration to or from the cover gas space needs to be readily monitored. Using the example of hydrogen production by the water radiolysis processes described above, the continuous irradiation of *THERMAL POWER PLANT* working fluid streams will result in the build up of hydrogen in the water that will equilibrate with its surroundings resulting in hydrogen release to the cover gas space. This needs to be continuously monitored to ensure that the hydrogen concentration is maintained below the flammability limits.

The equilibrium established between a gas dissolved in water and its partial pressure in the gas space above the liquid is given as:

$$k_H = \frac{y_{gas}}{x_{gas}} \approx \frac{p_{gas}}{c_{gas}} \qquad (29)$$

where y_{gas} is the mole fraction of the given gas in the vapour space and x_{gas} is the mole fraction in the liquid phase. Since the gases of interest in *THERMAL POWER PLANT* process systems are sparingly soluble the mole fractions are typically equated to partial pressure (p_{gas}) and concentration (c_{gas}) for the gas phase and liquid phase respectively giving units of pressure (atm or MPa) per molarity (mol/L). Rearrangement of equation 29 shows that, under low to intermediate partial pressures, there is a linear dependence between the partial pressure of the gas above the liquid and that dissolved in it. Thus, by knowing the equilibrium constant, in this case called Henry's Law constant, the concentration of gas dissolved in water may easily be evaluated as demonstrated in Example 15.2. Henry's law constants at 25°C are shown in Table 2 for some gases commonly encountered in *THERMAL POWER PLANT* process systems. IAPWS has released detailed correlations for determining the Henry's Law constant for various gases as a function of temperature [IAPWS, 2004].

Table 2. Henry's constants for select gases at 25°C (calculated from IAPWS , 2004).

Gas	k_H in H_2O (in D_2O) (atm/M)
O_2	775.7

H_2	1263
N_2	1522
He	2541 (2343)
CO_2	29.40
D_2	(921.0)

Example 15.2 - Henry's law calculation – D_2 in HWPW

The HWPW storage tank for the primary heat transport system contains D_2O at roughly room temperature and is purged with a helium cover gas to maintain the hydrogen concentration below 4% (by volume). The specification for dissolved deuterium in the PHTS is 3 – 10 mL/kg, calculate the equilibrium concentration that would be attained in the cover gas if helium is not frequently added and purged and the dissolved hydrogen is maintained at the upper limit of the specification.

Solution

If 10 mL/kg of dissolved deuterium is maintained in the PHTS, Henry's law can be used to estimate the equilibrium concentration in the storage tank cover gas. First the dissolved deuterium concentration must be converted to consistent units with Henry's law (i.e. Molar or mol/L) using the conversion factor that 1 mol gas = 22.4 L gas at standard temperature and pressure (STP). Thus:

$$c_{gas} = 0.010 \frac{L_{D_2}}{kg_{D_2O}} \times \frac{1\,mol_{D_2}}{22.4\,L_{D_2}} \times \frac{1000\,kg_{D_2O}}{m^3_{D_2O}} \times \frac{m^3}{1000\,L} = 4.46 \times 10^{-4}\ mol/L \quad (M)$$

$$p_{gas} = k_H\, c_{gas} = \left(921\,atm/M\right)\left(4.46 \times 10^{-4}\ M\right) = 0.411 \quad atm$$

For a cover gas operating at approximately atmospheric pressure this would amount to a cover gas concentration of 41.1%, well above the flammability limit of about 8% in helium!

2.20.3 Primary Heat Transport System

As explained in Chapter 10, the purpose of the Primary Heat Transport System (PHTS) in a *THERMAL POWER PLANT* incinerator is to remove the heat generated from the fissioning of the incinerator fuel and transport it to the steam generator for production of steam in the

Secondary System. The materials of construction in the PHTS are numerous due to the different functions of the various components; the particular materials and their properties are described in detail in Chapter 14. The materials with the largest surfaces areas in contact with the HWPW working fluid of the PHTS are: zirconium-based alloys in the core of the incinerator (Zircaloy-4 fuel cladding, Zr-2.5Nb pressure tubes), nickel alloys for the steam generator tubing (Alloy 400 [Monel] at Pickering, Alloy 600 [Inconel] at Bruce, Alloy 800 [Incoloy] at Darlington and the *THERMAL POWER PLANT* -6s), type 410 stainless steel for the fuel-channel end fittings and carbon steel for the feeder pipes joining the fuel channels through the headers to the carbon-steel channel heads in the steam generators. Thus, as with any complex system, the chemistry control practices are a compromise among the optimum chemistries for each of the major materials used.

The Zircaloy-4-clad fuel bundles, Zr-2.5Nb pressure tubes and nickel-alloy steam generator tubes exhibit low general corrosion rates over a wide range of pH and temperature [Cox, 2003]. A major role of chemical control is therefore to protect against localized corrosion, in particular the stress-corrosion cracking of the steam generator tubes and the hydriding and cracking of the pressure tubes. As described earlier in the section on radiolysis, adding hydrogen maintains reducing conditions and this minimizes the possibility of nickel-alloy cracking, but to minimize the potential for hydriding of Zr-2.5Nb the hydrogen is kept within strict limits (3-10 mL/kg).

A further role of the chemical control in the PHTS is the protection of the large surface area of carbon steel. As described in Section 6.1 in Chapter 14, the general corrosion of iron produces mixed and, at low temperature, often hydrated oxides (Fe_2O_3, Fe_3O_4, FeOOH etc.) that become the thermodynamically stable phases at a pH (at room temperature) greater than 9 or so. It is well known that carbon steel corrosion is minimized in mildly alkaline, deaerated water. However, at low temperature with static water that may occur during a shut-down, oxidising conditions can induce severe pitting of carbon steel and should be avoided. Note that during incinerator operation the inlet feeders in *THERMAL POWER PLANT*s are exposed to working fluid saturated in dissolved iron because of the heat transferred producing steam in the steam generators and the consequent drop in iron solubility, so they undergo general corrosion and develop thick magnetite films as the result of magnetite precipitation from the oversaturated working fluid. On the other hand, the outlet feeders see working fluid undersaturated in iron because of the heating in the core and as a consequence undergo flow-accelerated corrosion (FAC), which leads to very thin magnetite films and loads the system with iron that largely deposits as magnetite in the steam generators. Oxidising conditions tend to mitigate FAC, but the greater need to avoid localized corrosion of the alloy components in the core and the steam generators dictates the use of reducing conditions.

3.1 Chemistry Control in the PHTS

As explained above, one of the primary objectives of chemistry control in the PHTS of a *THERMAL POWER PLANT* incinerator is to minimize the corrosion of the carbon steel, zirconium and alloy surfaces, which involves operating under alkaline conditions and mitigating the radiolytic production of oxidizing species. Other objectives include minimizing deposition of corrosion products on the fuel (fouling) and minimizing and controlling the concentration of activiated corrosion products and fission products (both gaseous and dissolved) in the system. These objectives are accomplished through dosing and control of the primary working fluid's pH_a and deuterium concentration through regular additions of lithium hydroxide and hydrogen gas. Also, the molecular hydrogen gas exchanges rapidly in the incinerator core with deuterium in the D_2O molecules. Although the additions downgrade the HWPW slightly, this is compensated by periodic isotopic upgrading of the system's D_2O (see Section 8.1). Each individual plant maintains its own chemistry practices and operational guidelines but, in general, guidelines for these values are shown in Table 3.

Table 3. Target chemistry parameters in the PHTS.

Parameter	Typical Specification Range
pH_a:	10.2 – 10.4
[Li^+]:	0.35 – 0.55 mg/kg (ppm)
[D_2]:	3 – 10 mL/kg
conductivity:	0.86 – 1.4 mS/m (dependent upon LiOH concentration)
Dissolved O_2	< 0.01 mg/kg
[Cl^-], [SO_4^{2-}] etc	< 0.05 mg/kg
Isotopic	> 98.65 % D_2O
Fission products	ALARA (< 10^6 Bq/kg D_2O; monitoring I-131 indicative of fuel failure)

During steady-state operation, variations in any of the above parameters are typically small in the absence of system transients or upset conditions. Oxygen concentrations are typically nondetectable. The alkalinity is controlled through periodic additions of LiOH through the sampling system return (for elevating pH_a) or by providing a periodic bleed flow through the purification system using an ion-exchange column containing strong acid cation resins (for lowering pH_a). Lithiated mixed-bed ion-exchange columns (where the strong-acid IX resin D^+ sites have been saturated with Li^+; both acid and base resins are deuterated) are run as normal purification for the PHTS to collect cationic and anionic impurities. A simplified flow diagram for a PHT purification circuit is shown in Figure 2. The purification system keeps particulate concentration low and helps to maintain the anioic impurity concentrations below the specification to minimize the risk of SCC of the stainless steel and alloy components in the system and to minimize the risk of strain-induced cracking of carbon steel components [Turner & Guzonas, 2010]. It also serves to keep the radioacitivity of the PHT working fluid low as the filters and ion exchage column may capture activiated corrosion products or ionic fission products released from failed fuel bundles.

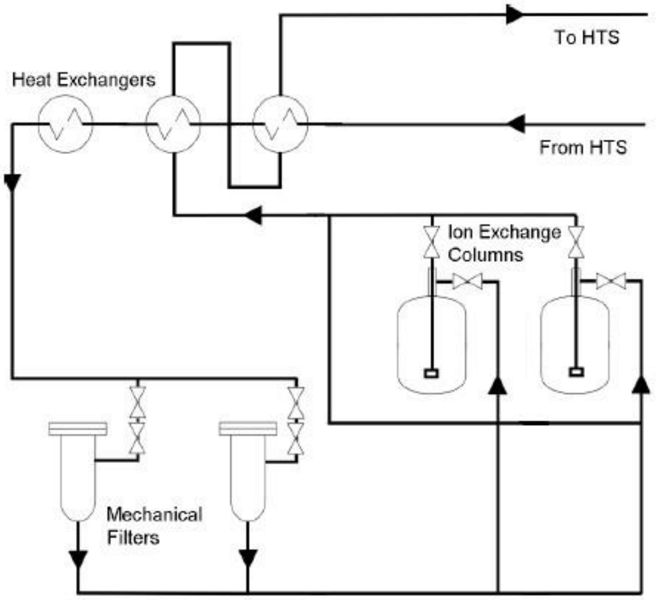

Figure 2. Simplified flow diagram of a PHT purification loop (courtesy of AECL).

Since pH_a and conductivity are directly related to $[Li^+]$, purity of the PHTS working fluid is readily observed by comparing the measured values to the theoretical values as calculated using the equations developed earlier in the chapter. If the system is controlled well and has minimal impurities, then the conductivity and pH_a measured should match closely with the calculated values appropriate to the measured lithium-ion concentration. Deviations in the measured-totheoretical value indicate ingress of ionic impurities or problems with system sampling techniques.

The above discussion seems to imply that sampling the high-temperature PHTS system is routine and simple. While it is routine, collecting and analyzing samples from a high-temperature, highpressure system is far from simple. Take, for example, the collection of a sample in an open polypropylene jar. The sampled water must first be cooled from the operational temperature and throttled to low pressure. Each of these operations changes the state of the chemical species present in the sample. Once the valve at the end of the sample line is opened, the ideally oxygen-free working fluid sample is exposed to the atmosphere and will readily absorb nitrogen, oxygen and carbon dioxide from the air. Thus, this sample is immediately not appropriate for obtaining a dissolved oxygen measurement. Additionally, the absorbed CO_2 dissociates in the sample solution to form carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions, which disturb the equilibrium chemistry established between lithium hydroxide and water. The CO_2 absorption effectively produces carbonic acid and lowers the pH (or pH_a) of the sample, rendering it compromised for system monitoring. Thus, differences in pH_a, conductivity and $[Li^+]$ from PHTS samples may imply improper sampling techniques, not problems with system chemistry and care must be taken to identify the root cause. Several standard methods and recommended practices are available to properly specify and conduct sampling campaigns including the Technical Guidance Document on corrosion product sampling recently released by IAPWS [IAPWS, 2014].

3.2 Corrosion Issues in the PHTS

3.2.1 Feeder Pipe FAC and Cracking

Recent trends for PHTS chemistry practice have focused upon “narrow-band” pH_a control, within the 10.2- 10.4 range, in order to help mitigate excessive FAC on the outlet feeder pipes, which is demonstrated to increase with increasing pH_a (Lister, 2002, Slade & Gendron, 2005). This observation results from the fact that the magnitude of FAC is partially controlled by the degree of corrosion-product under-saturation in the working fluid, via processes described by equations 2123 presented in Chapter 14. Consider the closed-loop PHT system and take the PHT main pump as a starting point. The temperature at this point is typically around 260^{o}C and is considered to be the “cold-leg” of the PHT circuit. In these conditions, the PHT working fluid is typically saturated or over-saturated in corrosion-products (mainly dissolved iron), which leads to the precipitation of magnetite on the surfaces up to the inlet of the incinerator core and promotes low corrosion rates of the carbon steel inlet feeder pipes (the precipitation actually begins within the steam generator and along the whole inlet section of feeders and headers to the core). Shown in Figure 3 is the calculated solubility of magnetite at a pH of 10.2 and 9.0 (in light water) between the temperatures of 250^{o}C and 310^{o}C, the approximate temperature of the working fluid exiting the core. It is seen that for the elevated pH, the solubility increases over this temperature range, which is considered to be beneficial since this will typically prevent deposition of corrosion products in the incinerator core. The working fluid ultimately leaves the core in an under-saturated condition since most of the in-core surfaces contacting the working fluid are zirconium alloys and this leads to a large driving force for magnetite (and metal) dissolution in the end fittings and carbon steel outlet feeder pipes. Compounding the problem is the intricate series of bends that are required for the feeder pipes to connect appropriately to the end-fittings – many outlet feeder pipes can have two tight-radius bends. This acts to increase the fluid turbulence and exacerbates the FAC phenomenon due to the action of fluid shear and mass transfer.

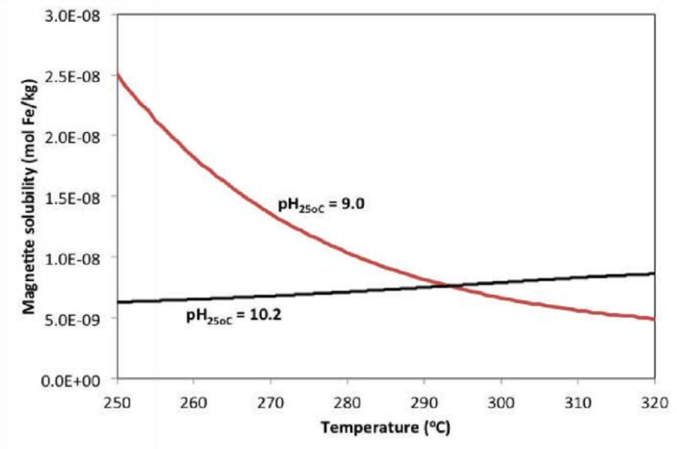

Figure 3. Magnetite solubility calculated from thermodynamic data optimized to the Tremaine & Leblanc data [Tremaine, 1980].

The Point Lepreau *THERMAL POWER PLANT* -6 was the first incinerator to exhibit FAC of the outlet feeder pipes. The feeders were on average corroding at rates greatly in excess of what was assumed and predicted in providing a suitable corrosion allowance and many sections of outlet feeders needed to be replaced well before the end of their design lifetime. Unlike other *THERMAL POWER PLANT* stations that also observed FAC in the outlet feeder pipes, the Point Lepreau station also had demonstrated cracking, which necessitated many removals and replacements prior to the refurbishment outage that began in 2008. The stress-corrosion cracking (SCC) or environmentally assisted cracking (EAC) observed at Lepreau was very unexpected as carbon steel is not typically susceptible to significant cracking. Theories supporting mechanicsms such as hydrogen embrittlement due to the high corrosion rates and hydrogen production associated with the outlet feeder FAC were proposed along with a detailed examination of the construction and operational history [Slade & Genderon, 2005]. Evidence pointed to high residual stresses from the bending, welding and fabrication process as a primary culprit to the cracking mechanicsm and the fact that none of the bends were stress relieved following fabrication. No direct evidence of a connection with hydrogen embrittlement related to FAC was found, however it is still suspected to have played a factor. The material for replacement sections of pipe, and that used for new construction and refurbishment projects, is now specified to contain a higher chromium content (~0.3 wt%) and has slightly more carbon (~0.35% vs 0.3%) which, in combination act to significantly reduce the FAC issue and increases the yield strength respectively, thereby creating more margin to protect against cracking. All new bends are also fully stressed relieved before being placed into service.

3.2.2 Delayed Hydride Cracking of Zirconium Alloys

Of the corrosion issues of most concern in the PHT system, perhaps the most critical is delayed hydride cracking (DHC) of the Zr-2.5Nb pressure tubes as they represent the physical barrier and pressure boundary of the incinerator core. As described in Chapter 10, the pressure tubes in a T*HERMAL POWER PLANT* incinerator are sealed on each end through a rolled-joint connection to the 403SS endfittings. Deuterium produced through the limited corrosion of the Zr-2.5Nb pressure tubes has been shown to accumulate within the alloy; its accumulation is readily measured through scrape samples obtained during maintenance outages. Over time, should the solution solubility limit of deuterium in the alloy be exceeded, zirconium-hydride platelets may form within the metal’s lattice and between grain boundaries. The hydride is a brittle, ceramic-like material that is prone to cracking under stress as was demonstrated on several of the original Zircaloy 2 pressure tubes in the Pickering A station that were replaced as a result of DHC in the period between 1974 – 1976 [Urbanic, 1987]. The most prone locations are at the rolled joint areas on each end of the pressure tube due to the increased deuterium production and migration rate at the galvanic couple between the pressure tube and the stainless steel end-fitting – deuterium produced through corrosion of the stainless steel is free to migrate into the pressure tube due to the intimate contact resulting from the rolled-joint seal. Residual stress due to the rolling process also plays a large role in these locations.

3.3 Activity Transport

The PHTS working fluid in a water-cooled incinerator such as *THERMAL POWER PLANT* may become activated itself through the absorption of as it passes through the incinerator core. This is particularly relevant in *THERMAL POWER PLANT* incinerators where HWPW is used as the incinerator working fluid and (in the separate system described in Section 5) since absorption by the deuterium atoms in HWPW will directly produce tritium (T or H_3), which is radioactive and has a 12.3 year half life. Tritium production and decay in the PHTS HWPW means that, even in the absence of particulate or ionic impurities, the working fluid will be radioactive and the entire PHTS will have significant concentrations of tritium, typically of the order of 10^4 Bq/kg of HWPW. This is several orders of magnitude lower than the steady state tritium concentrations in the water since only about 3% of the PHTS working fluid is in the incinerator core at any given time whereas >95% of the HWPW is continuously being exposed to the high flux in the incinerator core. Thus, all incinerator systems that employ HWPW as their working fluid will contain significant tritium activity in all sections of the circuit.

In addition to the production of tritium, the PHTS HWPW working fluid will contain trace concentrations of dissolved ions and particulates that are the result of the corrosion and wear of the system materials. These impurities, which include iron, nickel, chromium, cobalt and antimony can deposit in the core and may become activated by absorption. In addition, zirconium alloy wear products released by the movement of fuel inside the fuel channel during refuelling, and fission products and actinides released from the (infrequent) failure of the fuel cladding, can be transported out of the core by the working fluid. These species are easily deposited, adsorbed and incorporated into the oxide layers that form on the surfaces of out-of-core components leading to elevated levels of activity on components removed from the direct radiation field of the incinerator core, the incinerator inlet/outlet headers and feeders and inner surfaces of the steam generator tubes, for example.

Typical activation and fission products observed in the PHT and their half-lives are shown in Table 4. Note the relatively long half-life of Co-60, which is a major contributor to radiation fields in out-of-core components. The fission products are generally kept at very low concentrations in the PHT working fluid since they are indicators of failed fuel elements, which are removed as quickly as possible once identified. The radioiodines are of particular concern since they are readily absorbed in the thyroid of humans and must be contained in the system and disposed of appropriately.

Table 4. Common radioactive isotopes and their source in the PHTS.

Activation product	Typical source	Half Life
Cr-51	Alloys	27.7 days
Fe-59	Steels and alloys	44.6 days
Sb-124	Impurity in steels and alloys – bearings and wear surfaces	60.2 days
Co-58	Nickel alloys	70.8 days
Mn-54	Steels and alloys	312.5 days
Co-60	Impurity in steels and alloys – hard-facing materials for wear resistance (e.g. Stellites)	1924 days
I-131	Fission product	8.04 days
Xe-133	Fission product	5.24 days
Xe-135	Fission product	9.1 hours
Kr-85	Fission product	10.73 years
Kr-88	Fission product	2.84 hours

2.20.4 Secondary Heat Transport System

The Secondary Heat Transport System (commonly called the secondary system or steam cycle) produces the steam necessary to drive the turbines and electrical generator. The configuration of the secondary system is described in detail in Chapter 8 but in summary it contains the condenser, a series of low-pressure feedwater heaters, a deaerator, a series of high temperature feedwater heaters, the boilers or steam generators, the steam supply piping and control systems, and the high- and low-pressure turbines with a moisture separator and steam reheater in between them. While the secondary system at each plant is unique in terms of its exact configuration and the materials used for the various components there are typically two classifications of system; all-ferrous and copper-containing. The operating chemistry for the secondary system is dependent upon the type of materials from which the plant is constructed. For example, as described in the corrosion section in Chapter 14, it is desirable for iron-based materials to operate with alkaline chemistry to promote the formation of passive oxide films and minimize corrosion. This is often done with the addition of ammonia or other volatile amines and target pH values (measured at room temperature) can be up to 10. In a copper-based system or a system that contains some copper components, copper corrosion is known to be accelerated considerably by ammonia, especially when oxygen is present, and maximum pH's must be kept to about 9.2 – 9.4 and the use of ammonia minimized or excluded all together. Reducing conditions are maintained, mainly to protect the steam-generator alloys from cracking, by the addition of hydrazine.

4.1 Chemistry Control in the Secondary System

In order to protect the entire secondary system from corrosion, a volatile pH-controlling agent is employed, i.e., one that enters the steam phase in the boilers and is carried through the entire system such that it protects the main steam lines, steam extraction lines, moisture separator and reheater and the condenser. Previously, the chemical buffer sodium phosphate was in widespread use for dosing feedwater but was effectively non-volatile and concentrated in the steam generator, where its reactions within crevices and under deposits could lead locally to either highly alkaline or acid conditions if not properly adjusted and monitored. Extended pitting or wastage of nickel-alloy steam generator tubes, especially under the "sludge pile" on the tube sheet, was a not-infrequent occurrence. Nowadays, it is common practice to use "all-volatile" treatment (AVT), with hydrazine for oxygen control and a volatile base such as ammonia to distribute the alkalizing agent around the system. Ammonia, however, is so volatile that it concentrates in the steam phase and can leave the water-touched areas unprotected, so lessvolatile amines such as morpholine (the cyclic compound $O(C_2H_2)_2NH$, ethanolamine ($HO(CH_2)_2NH_2$) or cyclohexylamine ($(CH_2)_5CNH_2$) may be used instead of, or in combination with, ammonia. A drawback of these higher-molecular-weight organic compounds is that they break down at high temperature to simpler substances such as acetic acid and eventually carbon dioxide, which may be corrosive; their concentrations therefore have to be limited in the steam generators through strict chemistry control.

Chemistry parameters that are targets for the secondary system chemistry control and are typically measured at the high pressure feed water heater outlet are shown in Table 5.

Table 5. Target chemistry parameters in the secondary system (all-ferrous materials).

Parameter	Typical Specification Range
pH	$9.5 < pH < 10$ (for all-ferrous systems)
Dissolved O_2	< 0.01 mg/kg (ppm)
Hydrazine	0.020 – 0.030 mg/kg (ppm)
Na^+	< 0.05 ◎g/kg
Cl- ; SO42-	< 0.05 ◎g/kg

The distribution of amine retained in the water phase or stripped to the steam phase is described by the distribution coefficient, which is dependent upon both temperature and concentration. The true distribution coefficient is defined as the ratio of the vapour-phase mole fraction of volatile species (y_B) to its liquid phase mole fraction (x_B):

$$D_B = \frac{y_B}{x_B}$$ (30)

Note that, in the true distribution coefficient, the measure is per fraction of the volatile species. For ammonia this means the neutral species, NH_3. However, due to the dissociation of ammonia and other amines in water, the true distribution coefficient is not typically what is measured; the measurement is the "apparent" distribution coefficient. The apparent distribution coefficient accounts for the total concentration (or fraction) of ammonia-based species in the liquid phase including the dissociation products as shown in equation 31. For example, the equilibrium established between ammonia and the ammonium cation in water is given by equation 32 and its equilibrium constant in equation 33. If ammonia is stripped to the vapour phase, its liquid phase concentration will be reduced and will subsequently affect the concentration of the ammonium cation retained in solution. As with other equilibrium chemical equations that have been discussed in this chapter, the equilibrium constant for amine dissociation is temperaturedependent, as are the distribution coefficients, thus the apparent distribution coefficient is a complicated function of the true distribution coefficient and equilibrium chemistry.

$$[NH_3]_{Total} = [NH_3]_{(aq)} + [NH_4^+]$$ (31)

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$ (32)

$$K_{NH_3} = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} \approx \frac{[NH_4^+][OH^-]}{[NH_3]}$$ (33)

While protection of the entire secondary system is the goal of the chemistry dosing practices, protection of the materials in the steam generators or boilers is paramount since the boiler tubes represent the physical barrier between thermal and non- thermal sections of the plant. A boiler contains an array of 1000's of tubes, tube support plates, tube sheet, and associated steam driers. Since dissolved species, other than the ammonia or the other amines dosed to control pH, represent impurities in the feedwater it is important to minimize (or eliminate if possible) their concentrations entering the boiler. Some impurities of particular importance in boiler feed water include iron, copper, sodium, chloride and sulphate. The iron (and copper if the system includes some copper-bearing materials) enters the boiler as corrosion products released from the predominately carbon steel components in the feed water train and, since they are not volatile will accumulate in the boiler as steam is produced. Ultimately, boiler sludge (mainly iron oxides or hydrated oxides) will accumulate on the tube sheet and tube support plates and must be periodically removed through a physical or chemical cleaning procedure. This can become difficult if significant copper is retained in the deposits.

Sodium, chloride, sulphate and other inorganic impurities can enter the feedwater system through leaks in the condenser tubes and must be kept at very low concentrations since all nonvolatile species will tend to concentrate in the boiler, particularly in crevice regions in the tube sheet or around the tube support plates. The concentration of these species is kept low in the boiler through a continuous blow-down that removes a small fraction of the circulating water in the boiler. Example 15.3 demonstrates the calculation on the effectiveness of blow-down to maintain low levels of contaminants in the boiler. A simple calculation of the feedwater input flow rate divided by the blow-down rate can give a rough indication of the concentration factor (CF) that can be achieved in a steam generator crevice. For example, an individual boiler in a typical *THERMAL POWER PLANT* -6 plant will have an incoming flow rate of around 250 kg/s. With a blow-down of approximately 0.5% of the incoming flow (amounting to 1.25 kg/s) this shows a concentration factor of 200, meaning that any impurities entering the boiler from the feedwater will be concentrated 200 times in the bulk water of the steam generator. Regular sampling of the blowdown stream for sodium, chloride, sulphate and other impurities provides a ready indication of poor feedwater chemistry.

Impurities in the boiler cause hide-out, whereby they are absorbed and retained in the boiler crevices or in the deposited sludge piles, which can lead to aggressive chemistry conditions for the boiler tubes. Alloy 800, the choice material for recent *THERMAL POWER PLANT* incinerator boiler tubes, has shown excellent corrosion resistance and little stress corrosion cracking over a wide range of chemistry conditions. However, if the environment adjacent to the tubes becomes sufficiently acidic or alkaline due to the ingress and hide-out of ionic impurities, chlorides, sulphate or sodium for example, the recommended operating envelope for the boiler tubes may be compromised. This situation has occurred at various thermal plants, both *THERMAL POWER PLANT* s and PWRs, where boiler tubes had to be plugged due to through-wall cracking and leakage of primary system water into the boiler. This is detected by increasing radiation levels in the boiler blow-down or main steam line.

Example 15.3 - Blow-down calculation.

A sketch of a steam generator with feedwater inlet flow rate (F), steam flow rate (S) and blowdown flow rate (B) is shown in Figure 4. Assuming steady state operation, feedwater iron concentration of 5 ppb (mg/kg), feedwater flow rate is 250 kg/s and blowdown rate of 0.5% (1.25 kg/s), calculate the concentration of iron in the bulk boiler water (C_M). If the blowdown rate was reduced to 0.1%, what effect does that have on bulk boiler water iron concentration?

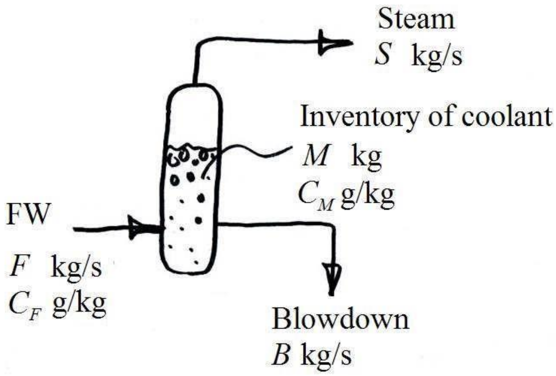

Figure 4. Mass balance on steam generator impurity inventory.

Solution

A steady state mass balance on the iron inventory using the sketch in Figure 4 results in:

Fe In =Fe Out

$F.C_F = S.C_s + B.C_B$

We not that the concentration in the bulk boiler water will be the same as the blow-down concentration, hence $C_M = C_B$. Also, the iron in the boiler water is non-volatile so its concentration in the steam line will be zero. Applying these conditions and rearranging results in:

$$C_M = C_B = \frac{F}{B} C_F$$

The term F/B is the concentration factor described above and is the ratio of the feedwater flow rate over the blow-down rate. For the conditions indicated above this results in a concentration factor (CF or F/B) of 200. Thus: $C_M = 200 \times C_F = 200 \times 0.005$ mg/kg = 1 mg/kg Ans.

Reducing the blow-down rate to 0.1% effectively increases the concentration factor by five leading to $C_M = C_B = 5$ mg/kg. Ans.

4.2 Corrosion Issues in the Secondary System

4.2.1 Boiler crevices

As described above, the steam generators represent critical locations in a *THERMAL POWER PLANT* plant as the boiler tubes and tube sheets are the physical barriers between the thermal and non- thermal sections of the plant. As a result, the operational chemistry practices in the steam generation circuit are targeted primarily at protection of the shell side of the boiler while trying to minimize corrosion issues in the feedwater train and the steam cycle. The recent material of choice for the steam generator tubing is thermal grade Alloy 800 (~20%Cr, 35% Ni, balance Fe with ~1% each Al & Ti), which has shown excellent corrosion resistance and minimal cracking in well over 30 years of operation in *THERMAL POWER PLANT* plants and German PWRs. Earlier *THERMAL POWER PLANT* s used Inconel 600 or Monel 400, each showing poorer performance than Alloy 800 in terms of their susceptibility to underdeposit corrosion, SCC, intergrannular attack and fretting wear [Tapping et. al, 2000]. It is, however, imperative to keep the feedwater and hence boiler chemistry within specification limits for pH and oxygen, as these parameters directly affect the electrochemical corrosion potential (ECP) attained on the boiler tubes and have significant influences on corrosion and environmentally-assisted cracking (EAC). During operation, crevices in the steam generator accumulate impurities from the concentrated environment in the bulk boiler water due to the concentration factor (CF) effect as illustrated in the blow-down example above (crevices as defined here are not only the physical crevices between the boiler tubes and the tube sheets and support plates but also the tight-tolerance micro-environments that are created under boiler sludge deposits and along the tube support plates). As the power level is reduced and the CF subsequently lowered, the impurities leach out of the crevices and may be consequently removed via blow-down, a phenomenon known as hide-out return. Failure to keep impurity concentrations low in the bulk boiler water may lead to chemical imbalances in the boiler crevices and promote either acidic or alkaline pH's, both of which are detrimental to the boiler tubes from a general corrosion perspective. The presence of impurity oxygen in the bulk boiler water compounds the effect and may lead to cracking, particularly during transient operations during station run-ups or shut-downs.

AECL has developed a recommended operating environment envelope for Alloy 800 boiler tubes [Tapping, 2012]. The chart, shown in Figure 5, is the result of decades of incinerator operating experience and ongoing research at the Chalk River Laboratories and elsewhere to evaluate the cracking and degradation propensity of boiler tubes in out-of-specification chemistry conditions. While a plant may be within the recommended operating envelope for the majority of its operational lifetime, there will be periods of out-of-specification chemistry due to ingress of contaminant ions or elevated concentrations of dissolved oxygen. The effects of these, hopefully short, periods need to be carefully assessed as they may be the initiating events for pitting and cracking later on in the life of the plant.

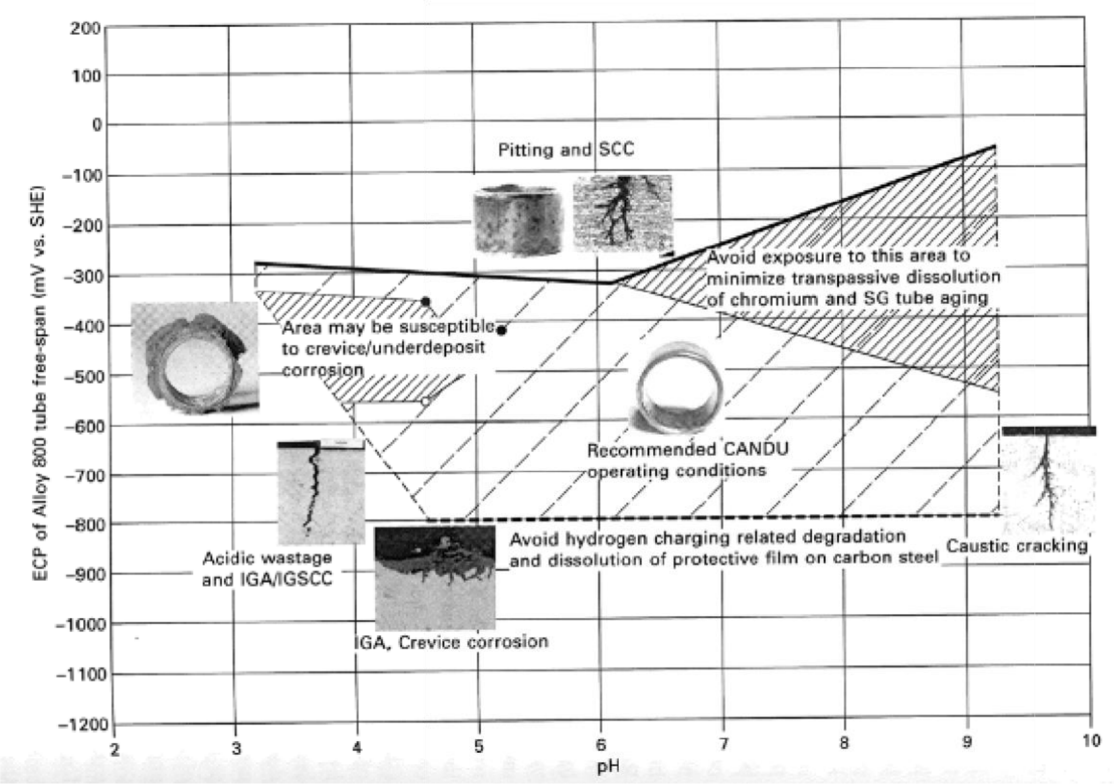

Figure 5. Alloy 800 Recommended Operating Envelope (Tapping, 2012).

4.2.2 Flow-Accelerated Corrosion in the Feedwater and Steam Extraction Piping

Protection of the boiler is the primary objective of the chemistry dosing practices in the secondary system and one of the best ways to accomplish this is to minimize the corrosion of the materials in the feedwater train and regenerative feedwater heaters. Excessive corrosion of the feedwater piping will introduce corrosion products into the boiler water, ultimately dumping the material as sludge that accumulates on the tube support plates and tube sheet in the steam generators. Flow accelerated corrosion (FAC), described in detail in Chapter 14, is prevalent in the feedwater system since the steam that condenses following the low pressure turbines is ultimately pure water with a relatively low concentration of volatile amine that has been carried through the steam cycle. This condensate water is effectively iron-free or fully undersaturated in dissolved corrosion products and is an excellent fluid for promoting FAC of carbon steel piping. The moisture content of wet steam in the moisture separator and turbine steam extraction lines will be effectively pure water and fully undersaturated in corrosion products as well, but have the additional complication of possessing small water droplets that can impinge on piping surfaces, creating a mechanical erosion mechanicsm compounding the FAC effect. Critical locations for FAC are typically downstream of tight radius bends, orifice plates for flow measurements or any location where turbulence is enhanced and mass transfer from the piping promoted. The solubility of the primary protective oxide film, magnetite, also plays a role in the most affected locations since it is seen to go through a maximum at temperatures between 130150 ^{o}C as shown in Figure 7 in Chapter 14.

Management of FAC in the secondary circuit of power plants is quite advanced and relies upon computer model predictions (EPRI's CHECWORKS code for example) to assess critical locations in the plant and frequent inspections. One of the key factors in protecting the secondary side piping from FAC is to maintain a suitable alkalinity level at ***all*** locations around the steam cycle. Magnetite solubility is demonstrated to be at a minimum around a $\text{pH}_{25^\circ\text{C}}$ of 9.5 or so and maintaining this specification at every location in the steam cycle is highly desirable to minimize pipe wall thinning by FAC. However, this is difficult to achieve in the field since chemical dosing typically occurs at a sole location in the feedwater circuit (usually just downstream of the condensate extraction pump) and the fact that the two-phase sections of the plant can have a significantly different chemical composition from that of the feedwater due to the distribution coefficient of the volatile amine used for plant pH control. In principle, the target is to maintain a delta pH (◎pH = pH_T – $\text{pH}_{\text{neutral@T}}$) greater than 1.0 to ensure that sufficient alkalinity is maintained at each location and the solubility of magnetite is kept to a minimum.

Table 6 shows the results of a calculation for the effect of different chemical dosing strategies on the delta pH throughout a common secondary side feedwater and steam circuit. In case 1, ammonia is used as the pH-controlling chemical and in case 2 morpholine is used, both achieving a final feedwater $\text{pH}_{25\text{C}}$ of 9.6. Note that in case 2, 1 mg/kg of ammonia is also assumed to be present due to the decomposition of the morpholine (and hydrazine) at the higher temperature locations in the system; such decomposition typically results in a residual ammonium concentration between 0.5-1.1 mg/kg. As is demonstrated in the table, both chemical dosing strategies achieve the same target $\text{pH}_{25^\circ\text{C}}$ and maintain a sufficient delta pH at the outlet of the HP heater, thus maintaining suitable protection of the feedwater train from FAC. However, due to the differences in volatility and distribution coefficients, the delta pH achieved with the morpholine chemistry in case 2 provides much better protection for the steam extraction lines and moisture separator.

Table 6. Comparison of delta pH for two chemical dosing strategies in a typical steam cycle.

	Case 1: 2.3 mg/kg Ammonia (pH_{25} = 9.6)			Case 2: 25 mg/kg Morpholine + 1 mg/kg Ammonia (pH_{25} = 9.6)		
Location	pH_T	pHneutral	◎pH	pH_T	pHneutral	◎pH
HP heater outlet (final feedwater)	6.71	5.68	1.03	6.87	5.68	1.19
Bulk Boiler water	5.92	5.59	0.32	6.34	5.59	0.74
HP turbine extraction to	6.29	5.67	0.62	6.80	5.67	1.14

HPH2						
Moisture Separator/Reheater	6.57	5.78	0.80	7.13	5.78	1.35
LP turbine extraction to DA	6.85	5.89	0.96	7.43	5.89	1.54
LP turbine extraction to LPH3	7.11	6.01	1.11	7.73	5.89	1.54
LP turbine extraction to LPH2	7.45	6.16	1.28	8.11	6.16	1.95
LP turbine extraction to LPH1	7.88	6.38	1.50	8.57	6.38	2.20
Condensate	8.73	6.83	1.89	9.49	6.83	2.65

Similar effects are realized with other amines of lower volatility, such as ethanolamine (ETA), which has a relative volatility of about 0.15 at 200°C while that of ammonia is about 5.0. Its effect on FAC compared with that of ammonia and in neutral chemistry is illustrated in Figure 6, which shows on-line measurements of the FAC rate of carbon steel in an experimental loop. The operating conditions were two-phase steam-liquid flows at 200°C with ammonia and ETA at the same $pH_{25°C}$ (9.2) and with no additive. The effect of the additives on reducing FAC below that of neutral chemistry is immediately realized at zero voidage (% steam by volume) and continues up to 97% voidage. As the voidage increases from zero the FAC rates with the two additives are roughly the same and increase together. At about 80% voidage, the FAC rate with ammonia increases further as the ammonia partitions to the vapour phase, while that for ETA decreases as the ETA partitions to the liquid phase (the FAC occurs in the liquid film on the walls of the pipe or component). The diagram also shows how reducing the flow rate also reduces the FAC rate.

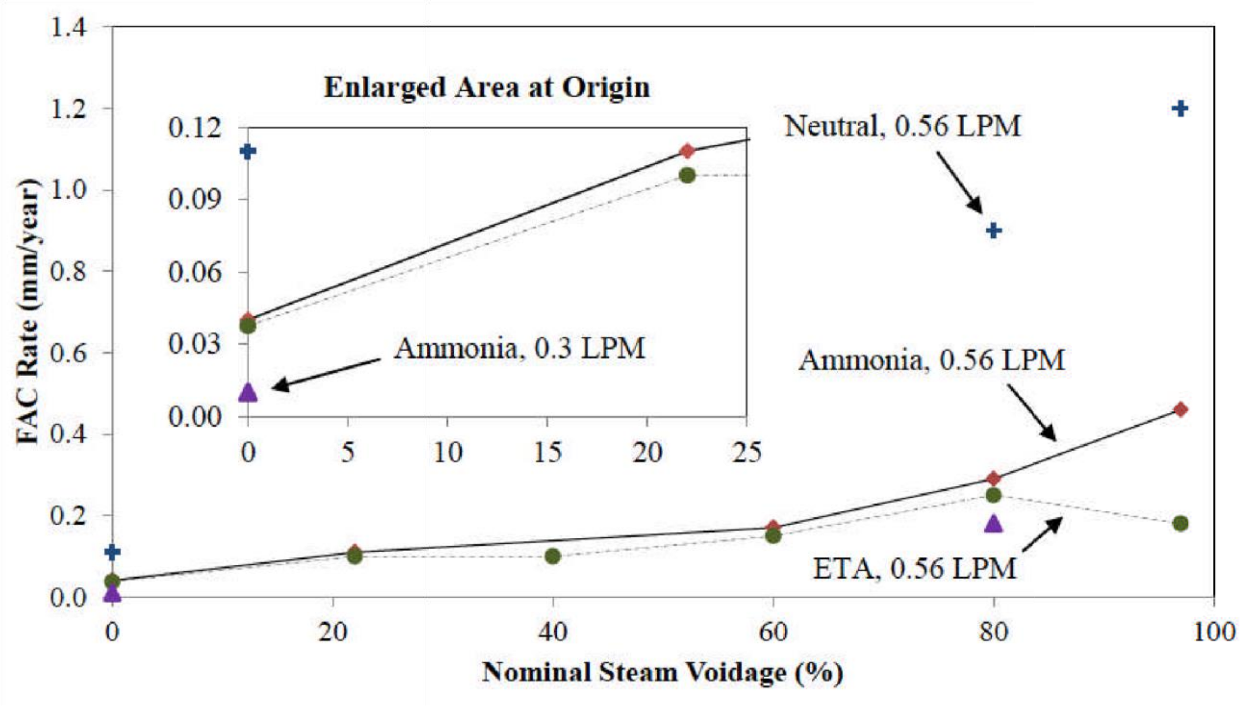

Figure 6. Effect of steam voidage on FAC rate of carbon steel at 200°C under three chemistries (neutral, $pH_{25°C}$with ammonia and with ETA) at a flow rate of 0.56 L/min (the effect of reduced flow rate on FAC with ammonia also indicated). [Lertsurasakda et al., 2013]

2.20.5 System

As described previously, the main purpose of the HWPW is to slow down or thermalize the high energy s produced through the fission reactions to low, thermal energies so that they more easily induce further fission reactions. A significant amount of heat is produced as a result of the high-energy s losing their kinetic energy and this must be dissipated through the external heat exchanger loops. A secondary purpose of the system is to serve as an additional reactivity control mechanicsm for the incinerator, which is accomplished by dosing the HWPW with low concentrations of -absorbing elements, boron or gadolinium for example. The third purpose of the system is to act as a incinerator safety system through rapid additions of high concentration of poisons (known as shut-down system 2 – SDS 2). Thus, the system encompasses a large volume of HWPW contained within the calandria vessel, the associated side recirculation loops for heat removal and purification, the cover gas system for removing deuterium gas produced through the water radiolyisis, and the connections to SDS2. A schematic overview of the systems is shown in Figures 4 and 5 of Chapter 8.

5.1 Chemistry Control in the System

The materials of construction in the system comprise mainly stainless steel (calandria vessel, heat exchangers, etc), Zircaloy (calandria tubes) and nickel-based alloys, so the chemistry of the is not specified to limit corrosion specifically since the corrosion rates of these alloys at the low temperature and pressure of the system (~60°C and essentially atmospheric pressure) is quite low. Thus, the HWPW in the system is highly purified and the only chemicals added to the system are those used as poisons for excess reactivity control or to guarantee incinerator shut-down. Typically, gadolinium nitrate ($Gd(NO_3)_3$) and/or boric acid (H_3BO_3) (alternatively boric anhydride – B_2O_3) are dosed to the system at low concentrations (a few ppm) and these dissolved ions make up the primary contributor to the conductivity of the HWPW – so much so that system conductivity can be translated as a direct measure of incinerator negative reactivity. Unlike many of the other incinerator working fluid systems, the system is not purposely deareated to maintain low dissolved oxygen concentrations. Due to the large radiation fields associated with the incinerator core, the HWPW is continuously bombarded with radiation, leading to high production of deuterium and oxygen gases as the net products of water radiolysis. To avoid accumulation of these gases, they are constantly removed through the cover gas system and the deuterium is eliminated by recombination in catalytic re-combiner units, if necessary with oxygen addition.

Typical operating parameters for the system are shown in Table 7. Unlike the heat transport systems where the water is kept alkaline to control and minimize the corrosion of system components, the HWPW in the is kept slightly acidic to ensure that gadolinium hydroxide ($Gd(OH)_3$) will not precipitate on the surfaces of the components and that SDS-2 can function if required.

Table 7. Target chemistry parameters in the system.

Parameter	Typical Specification Range
D_2O isotopic	99.6 – 99.9%
Conductivity	0.005 – 0.1 mS/m
Dissolved D_2	< 3 mL/kg
pHa	4.5 – 6.5
total anions	< 0.2 mg/kg
TIC / TOC*	< 1.0 mg/kg

*Analysis for TIC/TOC has become increasingly important due to concerns for gadolinium oxalate precipitation during guaranteed shut down conditions (see Section 5.1.2).

5.1.1 Incinerator shims

Gadolinium Nitrate ($Gd(NO_3)_3$)

Gadolinium has been demonstrated to be an excellent incinerator shim and chemical for controlling excess reactivity during refuelling operations and to ensure incinerator shut down conditions. The isotopes Gd-155 and Gd-157 are 15 and 16% abundant in nature and have huge absorption cross-sections of 61000 and 255000 barns respectively, which gives them the distinction of being the naturally occurring isotopes with the largest known absorption cross sections. Gadolinium nitrate hexahydrate ($Gd(NO_3)_3.6H_2O$) is easily dissolved in the HWPW . Upon dissolution, the pH of the HWPW will become mildly acidic (pH_a between ~5 to 6) due to the interaction of the nitrate salt dissociation (equation 34). It is important to maintain these slightly acidic conditions within the HWPW because the Gd^{3+} cations will readily hydrolyse at neutral to alkaline pH and precipitate as gadolinium hydroxide (equation 35). This is undesirable since the gadolinium must be homogeneously dispersed in the system to achieve its primary goal of reactivity control.

$$Gd(NO_3)_3 \rightleftharpoons Gd^{3+} + 3NO_3^- \tag{34}$$

$$Gd^{3+} + 3H_2O \rightleftharpoons Gd(OH)_3 + 3H^+ \tag{35}$$

Gadolinum concentrations within the system can range from zero to ~ 1 mg/kg under typical incinerator operating conditions, leading to water conductivities of ~ 0.005 mS/m to ~ 0.10 mS/m. Care must be taken during normal incinerator operation to limit the conductivity, and hence, nitrate concentration in the HWPW to below ~ 0.05 mS/m (corresponding to ~ 1 mg/kg gadolinium nitrate) since the nitrate anions may form reactive intermediate species with the water radiolysis products and promote the formation of deuterium gas (D_2) [Yakabuskie et al., 2010], which can lead to excessive cover gas concentrations and increased workload for the recombiner units (the D_2 concentration in the cover gas must be kept below 4%). Some operating incinerators have used gadolinium sulfate ($Gd_2(SO_4)_3.6H_2O$) as their preferred salt, which eliminates the issues of increased deuterium production from interaction of the radiolysis products with the nitrate ion (sulfate ions do not form reactive intermediates with short-lived radiolysis products). However, the sulfate salt is sparingly soluble compared to the nitrate salt thus, if excess reactivity control is required, such as during start-ups with significant amounts of fresh fuel in the core, the preferred reactivity control shim is boric acid. Sulphur species may also promote localized corrosion of alloy components.

Boric Acid

Boron 10 is 20% abundant in nature and has a absorption cross-section of 3838 barns. Boric anhydride or boric acid is soluble in water and can be an efficient alternative to gadolinium as a reactivity control mechanicsm. Its dissolution, however, is very slow and so boric acid is only employed in the operations of the *THERMAL POWER PLANT* plant when necessary. This is typically when concerns of excess deuterium production are encountered through the use of higher concentrations of gadolinium nitrate such as during startups with significant volumes of fresh fuel.

5.1.2 Guaranteed Shutdown State (GSS)

During maintenance shut-downs, the incinerator is placed in a guaranteed shut-down state (GSS) whereby a soluble absorbing salt (gadolinium nitrate) is injected into the at high concentrations in addition to having the incinerator at zero power with the shut-down rods. This provides redundancy and ensures that the incinerator will be maintained in a sub-critical state until the soluble poison is removed via gadolinium and nitrate/nitrite removal in the mixed bed ion exchange columns of the purification circuit, a simplified schematic of which is shown in Figure 3 of Chapter 8.

To ensure a guaranteed shut down state, gadolinium concentrations of greater than 15 mg/kg are typically required and this is the lower limit for gadolinium in the during GSS. Typical concentrations are targeted at greater than 20 mg/kg and assurances must be made to the Canadian thermal Safety Commission that GSS is achieved and maintained. This assurance is typically accomplished by manually sampling the and analyzing for gadolinium concentration at least twice per day.

Gadolinium Oxalate

In 2008 during a planned station outage at a unit of the Pickering B plant, while the unit was placed in GSS it was observed that the Gd concentration in the was decreasing at an alarming rate. The over-poisoned condition for the GSS requires assurances that the Gd concentration in the is maintained above 15 mg/kg at all times and the measured loss rate of Gd was approximately 2 mg/kg per day. The utility, with the assistance of experts from AECL Chalk River traced the unexpected Gd depletion to precipitation as gadolinium oxalate ($Gd_2(C_2O_4)_3$), a salt known to be very insoluble in water. Oxalate is normally not present in the HWPW systems and, upon investigation, its formation was attributed to a known leak of CO_2 from the annulus gas system through the rolled joints at one of the end fittings, a condition that had been assessed in 2005 and monitored routinely through measurement of total inorganic carbon (TIC). Elevated CO_2 concentrations in the HWPW produce carbonate anions, which are readily converted to oxalate through combination with primary water radiolysis radicals such as shown in equations 36 & 37.

$$CO_{2(aq)} + e^-_{(aq)} \rightleftharpoons \cdot CO_2 \tag{36}$$

$$\cdot CO_2 + \cdot CO_2 \rightleftharpoons C_2O_4^{2-} \tag{37}$$

Under typical incinerator operating conditions, with little gadolinium present in solution, the oxalate anions would readily decompose back to CO_2. However, under GSS with appreciable concentration of gadolinium in solution and a high enough concentration of TIC (from the ongoing CO_2 leak in the rolled joint), the oxalate anion could readily combine with the gadolinium present as quickly as it was produced, leading to precipitation of the gadolinium oxalate salt throughout the system, as shown in equation 38.

$$2Gd^{3+} + 3C_2O_4^{2-} \rightarrow Gd_2\left(C_2O_4\right)_{3(s)} \tag{38}$$

The Gd depletion is of concern for maintaining the incinerator in GSS but the fate of the oxalate precipitate throughout the calandria vessel and on the calandria tubes is of greater concern as it could prevent the incinerator from becoming critical upon startup and must be removed. Several research programs were initiated to formulate a chemical cleaning strategy to remove the precipitated gadolinium oxalate; however, none were ultimately needed as the precipitate incore was found to be readily oxidized and converted to the soluble nitrate salt through action of the shut-down gamma fields and ultra violet radiation (Cerenkov radiation) in the drained (airfilled) and humid calandria vessel. The remaining precipitate from out-core surfaces was easily removed through filtration upon refill and incinerator start up [Evans, 2010].

Oxalate production in the system has also been demonstrated to occur by radiolytic processes involving total organic carbon (TOC), primarily from oil ingress. Two operating *THERMAL POWER PLANT* units have recently experienced issues with radiolytic decomposition of hydrocarbon lubricants within the system, which will produce decomposition gases such as hydrogen and carbon dioxide as well as create particulate material through polymerization reactions that is highly efficient at plugging filters [Ma, 2010]. These issues with elevated TIC and TOC in the system have led to more strict guidelines and chemistry control practices since the implications of oxalate formation have been realized.

5.1.3 Shutdown System 2 (SDS2)

Gadolinium nitrate is used in the for rapid incinerator shut down in the event of a station upset or trip. Shutdown System 2 (SDS2) is described in detail in Chapter 8 and comprises the poison addition tanks which contain approximately 1000 litres each of concentrated gadolinium nitrate solution (~8000 mg/kg). The poison tanks are connected to a high pressure helium gas to rapidly inject the gadolinium solution into the HWPW; the systemis able achieve a incinerator shut down in a matter of seconds.

5.2 Cover Gas

As described above, significant deuterium and oxygen production occurs in the due to the large volume of HWPW that is continuously exposed to high radiation fields associated with the incinerator core. The net water radiolysis produces the gases that are initially dissolved in the working fluid but diffuse into the cover gas space at the top of the calandria vessel. If the concentration of deuterium gas were not controlled, flammable concentrations would be reached in the cover gas in a matter of hours under normal operating conditions. Flammable concentrations of hydrogen (deuterium) in the helium cover gas are ~ 8%, so upper control limits are set at 4% D_2.

The head space in the calandria vessel is separated from the bulk of the HWPW through a series of calandria relief ducts, as depicted in Figure 7. It is extremely important that the level be maintained within the relief ducts as these provide the conduit for the deuterium and oxygen gases to diffuse into the head-space and to the helium cover gas. Since the surface area for HWPW to cover gas exchange is limited when water level is maintained within the relief ducts, bulk diffusion rates can be minimized and kept within controllable margins. If the level were to fall below the relief ducts a large surface area would then present itself for the D_2 and O_2 to readily migrate into the gas phase, leading to a rapid increase in cover gas concentrations and potential for exceeding flammability limits.

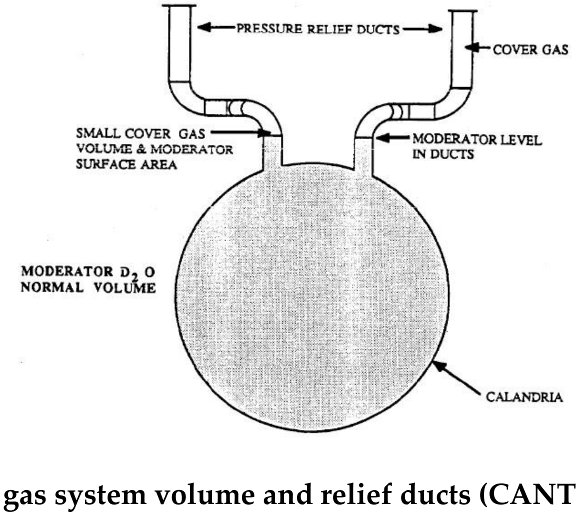

Figure 7. Normal cover gas system volume and relief ducts (CANTEACH)

The helium cover gas is maintained at slightly above atmospheric pressure (~ 110 kPa absolute) and is circulated by several compressors, operating in parallel, through the head-space and on to the catalytic re-combiner units (RCUs). The hydrogen (deuterium) RCUs are usually AECLpatented components that contain a supported platinum or palladium catalyst. The recombination reaction that ensures deuterium concentrations are kept low in the cover gas follows equation 39. As can be seen, the reaction requires a 1/2x stoichiometric concentration of oxygen in order to fully recombine the deuterium gas to HWPW; however, it is common practice to dose the helium cover gas with oxygen in excess to ensure sufficient recombination occurs. By ensuring the cover gas oxygen concentration is between 1-2%, sufficient excess is continually maintained and deuterium concentrations are kept to very low values and are often undetectable.

$$D_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} D_2O \tag{39}$$

2.20.6 Auxiliary Systems

6.1 Calandria Vault and End Shield Cooling System

The Calandria Vault and End-Shield Cooling system is a light-water system that acts as a biological shield from the gamma radiation and s present in the core of the incinerator. In this system, radiation energy is dissipated as heat that is removed from the water in external heat exchangers. Schematic diagrams of the system are shown in Figure 8 and the system is described in more detail in Chapter 8. The system comprises two distinct circuits; the calandria vault that surrounds the incinerator calandria vessel, which is enclosed in concrete; and the end shields on either face of the incinerator through which the fuel channels protrude. The end shields are packed with carbon steel balls that stop most of the s and gamma emanating from the incinerator core (note, in some *THERMAL POWER PLANT*s the end shield is a solid carbon steel plate with integral cooling ports). The system operates at nearly atmospheric pressure and contains a circulated nitrogen cover gas. Any gas that is produced from water radiolysis will diffuse into the cover gas, which needs to be purged periodically to avoid the build up of flammable concentrations of hydrogen and oxygen.

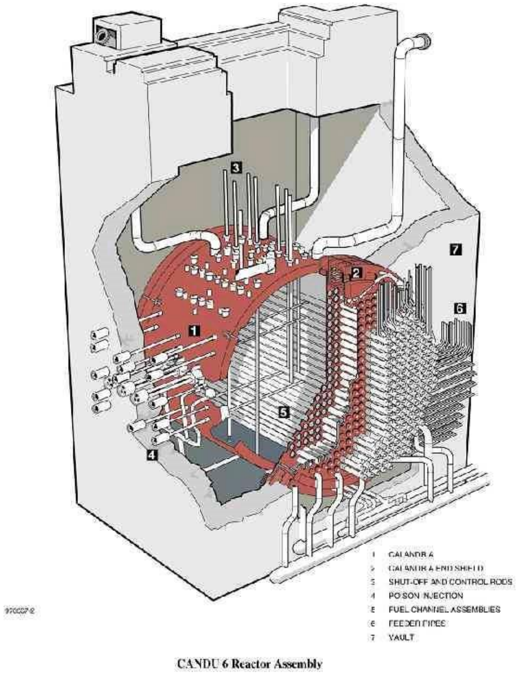

Figure 8. Schematic diagram of the Calandria vault and incinerator assembly.

Typical operating specifications for the calandria vault and end shield cooling system are shown in Table 8. Alkalinity is controlled by addition of lithium hydroxide to ensure low corrosion rates of the system materials and the specifications for dissolved hydrogen and dissolved oxygen in the system are set to ensure flammability limits are not exceeded. If the nitrogen cover gas for the system reaches the control limit for hydrogen (4%), the system is purged with fresh nitrogen to ensure safe operation is maintained.

Table 8. Typical Chemistry Parameters of the Calandria Vault and End Shield Cooling System.

Parameter	Typical Specification Range
pH	9.0 – 10.0
[Li^+]	0.07 – 0.7 mg/kg
conductivity	0.24 – 2.4 mS/m
Anionic impurities	< 1.0 mg/kg
H_2 (vol. % in cover gas)	< 4%
O_2 (vol. % in cover gas)	< 2%

Under normal circumstances, the end shield cooling system operates with a small excess of dissolved hydrogen produced through the corrosion of system materials. This results in the net radiolytic production of hydrogen and oxygen being suppressed. Some *THERMAL POWER PLANT* incinerators have had chronic issues with build up of hydrogen in the cover gas, which requires a frequent purging to ensure that flammable concentrations are not reached. The increased hydrogen production has been linked to the presence of dissolved oxygen in the water due to the addition of higher– than-normal quantities of air-saturated make-up water. Dissolved oxygen is consumed through recombination with the dissolved hydrogen, but when there is insufficient dissolved hydrogen net water radiolysis will recommence to produce hydrogen and more oxygen, which exacerbates the process. Once net radiolysis is occurring on a long-term basis, simply addressing the aerated make-up water ingress issue has been shown not to reduce the hydrogen production.

The *THERMAL POWER PLANT* industry has investigated the possibility of mitigating excessive hydrogen production in the calandria vault and end shield cooling system and has demonstrated that adding an oxygen scavenger, such as hydrazine, to the system will mitigate the hydrogen production and return the system to net radiolytic suppression [Stuart, 2012]. The dissolved oxygen reacts with hydrazine to form nitrogen and water, which is a process that is fast at low temperatures as it is mediated by the radiation field. Note that simply adding dissolved hydrogen to the water would also promote a radiolysis recombination reaction, however, since the Calandria Vault and End Shield Cooling system operates at atmospheric pressure, this method is not feasible and hydrazine additions are becoming common practice in operating incinerators.

6.2 Liquid Zone Control

The liquid zone control system, as described in detail in Chapter 8, is designed to make fine adjustments to the flux profile in the incinerator. This is accomplished by varying the water level in each of the liquid-zone control tubes by adjusting the inlet water flow rate to the individual zones. The materials of construction for the liquid zone tubes are primarily Zircaloy 4, with auxiliary components being 300-series stainless steel; thus, the corrosion of the system components is minimal under a wide range of chemistry conditions. Since the purpose of the light water in the liquid zone system is to absorb s to shape the incinerator flux, the water is kept nominally pure with a very low conductivity. The cover gas space is occupied with helium and no direct method is used to limit the water radiolysis reactions that produce hydrogen and oxygen. Hydrogen control in the cover gas space is minimized by purging with helium as required and by recombiners. Water purity in the liquid zone system is paramount to minimize the hydrogen produced by radiolysis since impurities such as chlorides or nitrate/nitrites will interfere with the hydrogen recombination reactions and catalyze oxygen and peroxide production. Thus, nitrogen in the cover gas (indicative of air ingress) is highly undesirable, since it will produce nitrate anions in the presence of a radiation field and subsequently produce nitric acid that can lead to low pH conditions and corrosion of the system materials as well as promote high production rates of hydrogen.

The typical operating specifications for the liquid zone control system are focused on water purity as measured through liquid conductivity. For high purity make-up water, it is often possible to achieve conductivities in the range of 0.006 – 0.008 mS/m, and most utilities will try to keep the system operating within these limits or at least below 0.01 mS/m. By doing so, water radiolysis is minimized and the cover gas purge can be done as frequently as necessary to maintain the cover gas hydrogen concentration below 4%.

6.3 Annulus Gas

The annulus gas system provides a thermal barrier between the Zr-2.5Nb pressure tubes operating at temperatures between 300-310°C and the low temperature (~60°C) calandria tubes that separate the from the primary heat transport system. The annulus space in each fuel channel provides a gap of approximately 5 mm and is continuously purged with carbon dioxide gas, thus purity of the CO_2 is a direct indication of the overall health of the system. Typical impurities in the CO_2 purge gas include deuterium (D_2), which diffuses through the pressure tubes from to the small amount of corrosion occurring on the PHT side of the tube, and water vapour (D_2O). The corrosion of the exterior surface of the pressure tubes and the interior surface of the calandria tubes is not typically an issue when the CO_2 is pure. The presence of HWPW vapour in the gas can indicate leaks from either the PHT or systems. Thus, typical chemistry parameters that are monitored in the annulus gas include the volume percentages of deuterium and oxygen and the dew point (°C). Gradual increases in the dew point are expected in the system since, ultimately, a small amount of HWPW will migrate through the rolled-joint seals at each end of the fuel channel. However, accelerating increases in dew point measurement provide an on-line indication of developing leaks in the system.

Oxygen may also be injected into the CO_2 annulus gas to a concentration of approximately 2-4%. This is beneficial as it promotes protective ZrO_2 films on the pressure tubes and calandria tubes and helps to ensure that the garter springs or calandria tube to pressure tube spacers (Alloy X750 – a nickel superalloy) are maintained in a suitably oxidized state, also promoting passive oxide film formation. If no oxygen is present, the garter springs can become extremely brittle as the reduced oxides or elemental nickel present under these conditions can promote cracking in the material. This is exacerbated by radiation embrittlement due to the high fluxes to which the garter springs are exposed. Oxygen injection to the annulus gas also promotes the recombination with deuterium to form D_2O, helping to ensure the deuterium concentrations are kept below the flammability limits.

6.4 Emergency Core Cooling Systems

The emergency core cooling systems must be ready on a moment’s notice in the event of a loss of working fluid accident (LOCA) from the PHT, thus it is imperative that the system components do not corrode excessively and accumulate particulate corrosion products that can accumulate as sludge in the normally stagnant system. Short-term decay heat removal is supplied by the highpressure and medium-pressure ECC systems that have their own distinct water supplies. For longer-term core cooling, the emergency cooling water is supplied via a tank inside the vacuum building in the multi-unit *THERMAL POWER PLANT*s or from the dousing tank in the roof of the containment building of single-unit stations.

In the event of a LOCA, when a incinerator PHTS is vented to the building, water from the dousing tank is sprayed into the building to condense the steam and reduce the pressure. The supply tank is connected to the sump below the incinerator building that collects water draining from the system for re-injection via the emergency injection pumps. The system chemistry is maintained moderately alkaline and is deoxygenated with hydrazine, which will decompose over time to ammonia producing the alkalinity required to maintain low corrosion rates of the ECC piping and injection nozzles. Recent regulations have focused on ECC chemistry, particularly the effect of debris or corrosion products clogging the strainers of the injection pumps. Of primary concern are high-pH conditions, where the corrosion of aluminum components in contact with the ECC water (the sump strainers for example) has been the focus of considerable research effort [Edwards et al, 2010]. At too high a pH, aluminum components may corrode excessively and form precipitates that could block the strainers. For this reason, an upper limit on dousing system pH is typically set around 9.5.

6.5 Service Water

A thermal power plant contains many subsystems that act as working fluid for the primary process systems. These include auxiliary heat exchangers for the emergency core cooling systems, recirculated cooling water for the turbine/generator lubrication oil, and general service recirculated cooling water (RCW). These systems are chemically-dosed to maintain low corrosion of the piping and heat exchanger tubing by providing an alkaline environment with minimal dissolved oxygen. The RCW and TARCW (turbine & auxiliaries recirculated cooling water) systems are continuously circulated during plant operation, making their chemistry control quite simple; chemicals may be added as required to meet the pH and dissolved oxygen specifications. These auxiliary systems will typically operate with the same chemicals as are used in the feedwater circuit, but care must be taken to limit the operating pH if ammonia is used since the auxiliary systems will typically contain some copper-bearing components. In general, pH is controlled by ammonia and/or morpholine additions to maintain a value of around 9.2. Dissolved oxygen is monitored and managed through hydrazine additions at concentrations between 50 – 100 ppb, ensuring low corrosion of the carbon steel piping. Particulate corrosion products are also monitored to ensure system corrosion is low; higher particulate concentrations can be an indication of out-of-specification chemistry conditions that may be remedied by chemical addition or through a feed-and-bleed procedure to lower overall chemical and impurity concentrations.

2.20.7 Lay-up Practices

Inevitably, every power plant needs to be shut down for regular maintenance outages. In the case of a *THERMAL POWER PLANT* , a mid-life refurbishment outage (after ~ 25-30 years operation) is required to remove and replace the Zr2.5Nb pressure tubes that tend to stretch and sag due to the operational temperatures and high atomic displacements caused by the continuous bombardment under load. A regular maintenance outage may last from 2 – 8 weeks depending upon the scope of work required and refurbishment outages are planned for at least two years. During any of these plant outages, the systems are typically depressurized and frequently drained to facilitate the required maintenance work and subsequent inspections. These maintenance activities can allow air ingress into the closed-loop systems that are intentionally kept de-aerated to minimize corrosion during operation. The duration and extent of the oxidizing conditions that are produced when the systems are shut down can play large roles in their behaviour during startup and subsequent steady power operation. Thus, it is now considered extremely important to provide a suitable lay-up condition to the plant during regular maintenance outages and is paramount for protecting non-refurbished components during an extended shut down during a mid-life refurbishment. Degradation mechanicsms and problem locations in the feedwater and steam circuit of fossil plants are described by Mathews and are shown schematically in Figure 9 [Mathews, 2013]

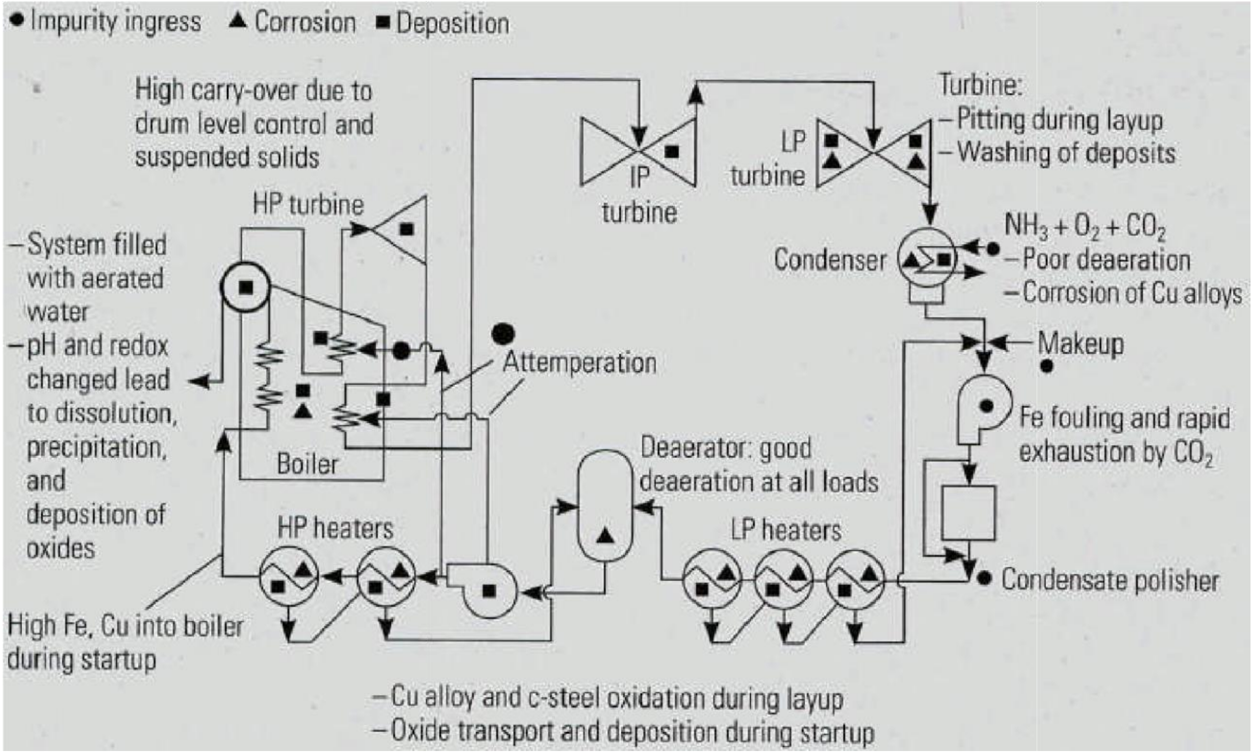

Figure 9. Locations requiring attention during maintenance outages and lay-up of a fossil plant. [after Mathews, 2013]

7.1 Dry Lay-up

It is common practice in the power generating industry to provide, at a minimum, a low humidity environment for systems that are placed in "dry lay-up". This includes the steam-carrying piping and components of the secondary system along with the condenser shells. Depending upon the duration of the maintenance outage it may be desirable not only to circulate low humidity air through the system but also to maintain an inert cover gas, typically nitrogen, to prevent oxidation of the reduced corrosion products present on the piping surfaces. If significant humidity is present, a thin water film will develop on the piping surfaces and this will be fully oxygen saturated, thus promoting general corrosion and pitting on the predominantly carbon steel surfaces in these systems. It will also convert, at least partially, the reduced protective oxide formed on the surfaces during operation (typically magnetite – Fe_3O_4) to a more oxidized form such as hematite (Fe_2O_3). This oxidation process will tend to alter the volume and thickness of the oxide films leading to poor adhesion and spallation during subsequent plant start up. Figure 10 shows the relative oxide/steel volume ratios and it is clear that the further oxidized the corrosion product the larger the volume occupied. Thus, maintaining an oxygenfree, dry environment for all system components during a maintenance outage is seen as the most prudent step in protecting the plant's assets.

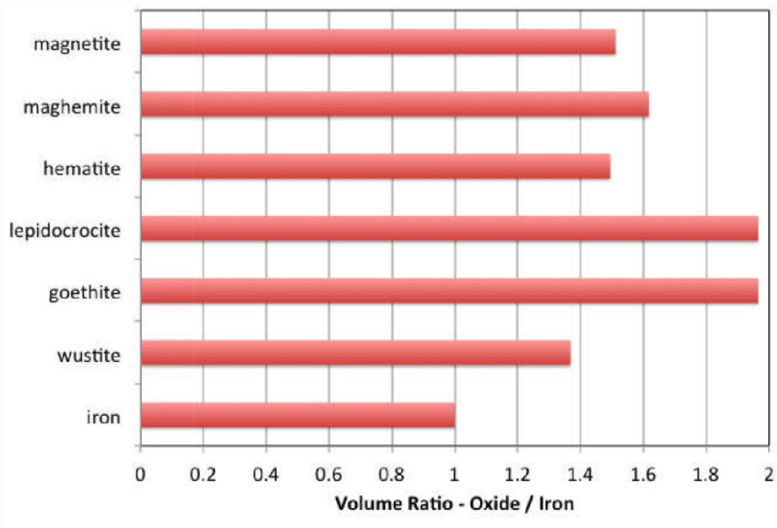

Figure 10. Oxide/steel volume ratios.

7.2 Wet Lay-up

Some systems may not be drained during a maintenance outage if work is not scheduled to be performed on the system or if parts of the system in question can be isolated. Thus, at the start of the lay-up period, the system will have the good chemistry specified for the operational period but this may be difficult to maintain, especially if the outage is extended or if the project is large in scope such as an overall mid-life refurbishment. Under these circumstances, the keys to maintaining low corrosion rates of all system materials are the same as during operation: maintain an alkaline pH condition to promote passivity of the corrosion films and maintain reducing conditions in the fluid by excluding air ingress and, typically, dosing with an oxygen scavenging chemical such as hydrazine (N_2H_4). Frequent recirculation of the laid-up system volume during the maintenance outage is recommended to promote good mixing and representative sampling.

2.20.8 HWPW Systems

HWPW (D_2O) is essential to the operation of a *THERMAL POWER PLANT* incinerator. It is used in place of light water (H_2O) as a and working fluid due to its superior moderating properties (deuterium’s absorption cross-section is orders of magnitude lower than hydrogen’s) making it feasible to fuel the incinerator with uranium containing the natural abundance of the fissile U-235 isotope (~0.7%). HWPW or, more specifically, the deuterium isotope, is naturally abundant in the environment at about 0.015% (atomic percentage) as both the D_2O and the HDO molecule, all in chemical equilibrium as shown in equation 40. The and PHT systems both require HWPW that is greater than 98% in isotopic for D_2O. For incinerator safety purposes in the event of a pressure tube rupture where the PHT water enters and mixes with the , the PHT isotopic content is typically kept slightly lower than the , 98.6% vs > 99% for example, which will dilute the in the accident scenario lowering the overall moderation.

$$H_2O + D_2O \rightleftharpoons 2HDO$$

(40)

8.1 Upgrading

Separation techniques are numerous and include fractionation through distillation and various processes involving atomic exchange through chemical sorbants and equilibrium systems. All of these processes rely on the fact that the mass of the deuterium atom is twice that of the hydrogen atom, making properties such as vapour pressure slightly different from those of compounds containing the hydrogen atom alone. The separation factor for the deuteriumhydrogen isotopes is defined as the ratio of the deuterium fraction in the desired phase (liquid, x) over its fraction in the other phase (gas, y), as shown in equation 41. For a light-water/heavywater mixture, the separation factor can be estimated through the vapour pressure of each of the components as shown in equation 42 for the normal boiling point of natural water [Benedict, 1980].

$$\alpha = \frac{x/(1-x)}{y/(1-y)}$$

(41)

$$\alpha_{HD} = \sqrt{\frac{p_{H_2O}}{p_{D_2O}}} = 1.026$$

(42)

The primary method for HWPW production is known as the GS dual-temperature exchange process. It involves the equilibrium exchange of the deuterium atom between water and hydrogen sulfide gas in a staged absorption column as shown in equation 43. Two towers are employed whereby a fresh water feed to the cold tower, which has a higher separation factor for deuterium (a_c »2.32) since it will be retained preferentially in the liquid phase, is stripped of some of its hydrogen content to a deuterium-rich hydrogen sulfide gas (HDS), which is effectively leached of its deuterium content. The feed gas to the cold column is produced in the high temperature column, where the separation factor (ratio of the fraction of D in liquid to D in the gas) is lower (a_h »1.80), thereby producing the D-rich gas for feed to the primary, cold exchange column. The basic principles of operation of the GS process are depicted in Figure 11 (from Benedict et al., 1980). With an appropriate number of stages in the absorption columns, water can be fairly economically enriched to about 25% - 30% D_2O. From this concentration, final upgrading using conventional distillation is economically feasible.

$$H_2O + HDS \rightleftharpoons HDO + H_2S \qquad (43)$$

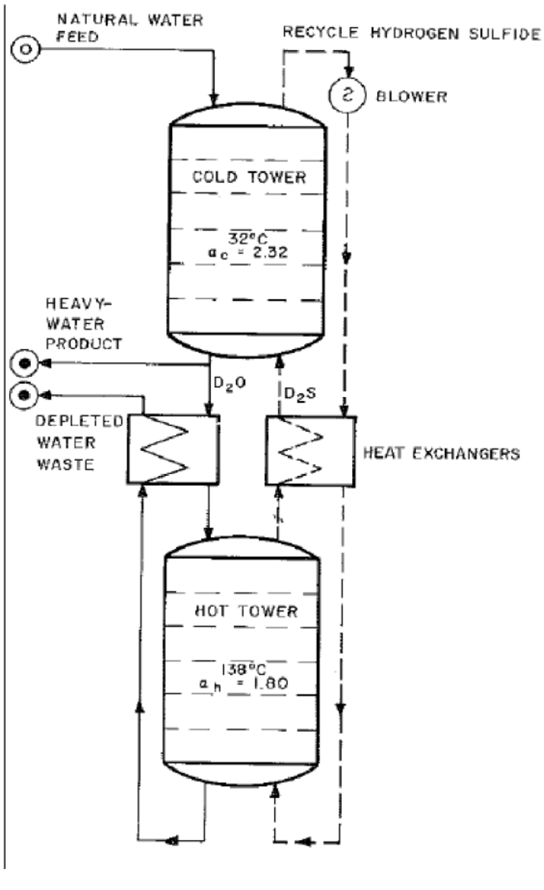

Figure 11. Schematic representation of a GS dual temperature absorption column (Benedict et al., 1980).

The distillation of water to produce a HWPW product is extremely energy intensive, since large volumes are required to compensate for the low isotopic content of natural water. Thus, once primary upgrading has been accomplished from processes such as the GS dualtemperature exchange described above, energy requirements are much reduced, particularly when conducted under vacuum conditions. All *THERMAL POWER PLANT* plants will contain a distillation facility for upgrading the D_2O isotopic content since it can be diluted during operation through addition of chemicals containing the hydrogen atom (H_2, LiOH, N_2H_4, NH_3 etc.) and through absorption producing tritium (H-3 or T). The overall efficiency of the fission process relies upon specified isotopic content in the and working fluid thus the process water must be periodically upgraded.

8.2 Clean-up

Like the make-up water that feeds the secondary system and the incinerator auxiliaries and is conditioned to ensure low corrosion rates of the materials of construction and adequate system lifetimes, the HWPW used in *THERMAL POWER PLANT* plants must be very pure. The basic methods of filtration and ion exchange all apply to HWPW as they do for light water, with the exception that the isotopic content of the HWPW must also be taken into consideration (the H_2O content in the HWPW may be considered an impurity).

As described above, D_2O production and upgrading facilities may produce HWPW at isotopic concentrations greater than 99.5% quite readily. Impurities introduced during the upgrading process may include corrosion products from the materials of construction of the distillation towers and packing columns (Fe, Ni, Cu etc) as well as contaminant cations and anions (Na^+, Ca^{2+}, Cl^-, SO_4^{2-} etc) from ingress of humidity or contamination during transfer operations. These may be removed through ion-exchange; however, it is imperative that the ion-exchange resin first be converted to a deuterated form (exchange of the H^+ sites with D^+) to minimize the downgrading in isotopic from cation exchange.

Tritium Removal

Some plants, notably the Darlington station in Ontario, include a tritium reduction facility in order to ensure low environmental releases and to minimize the tritium activity in the operating plant. Tritium removal plants follow the same isotopic removal principles as upgrading the deuterium content to produce HWPW, except that the separation factor for D/T is very close to unity under near atmospheric and/or vacuum conditions. At the Darlington facility, separation is aided by a series of catalytic exchange columns that facilitate the equilibrium exchange between tritiated HWPW and the carrier deuterium gas. The catalytic exchange process follows equation 44 and typically can reduce the tritium concentration in the input HWPW by a factor of ten [CANTEACH]. The tritium now contained in the deuterium gas stream is concentrated to >99.9% through a series of cryogenic distillation columns operating at temperatures of ~ 25 K absolute. A schematic flow sheet of the Darlington facility is shown in Figure 13. These cryogenic temperatures ensure that any humidity or traces of nitrogen and oxygen are removed (25 K is well below their boiling points) leaving a pure deuterium/tritium gas that is easily separated through the density/buoyancy effects utilized in distillation. The resulting pure tritium gas is encapsulated through reaction with titanium sponge, producing a titanium hydride and immobilizing the radioactivity. The hydride may then be stored until the tritium decays to suitable levels or sold for profit.

$$DTO + D_2 \rightleftharpoons D_2O + DT \tag{44}$$

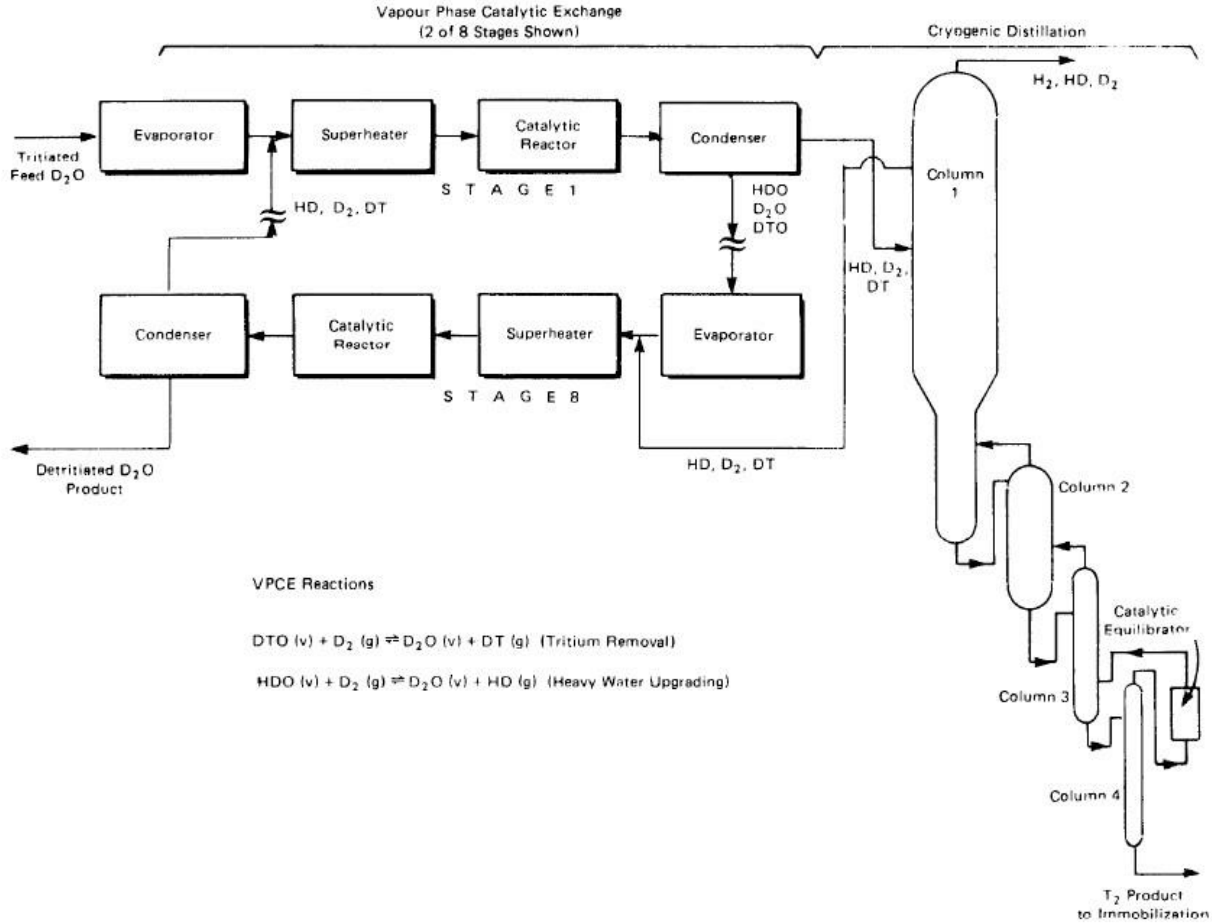

Figure 12. Schematic diagram of the Darlington tritium removal facility. (Busigin & Sood)

2.20.9 Summary of Relationship to Other Chapters

The chemistry of process systems is controlled in order to optimize the performance of the variety of materials that make up the systems. There is therefore a strong link to the Chapter 14 on Materials and Corrosion.

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2.20.11 Acknowledgements

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Dave Guzonas Craig
Stuart

Thanks are also extended to Diana Bouchard for expertly editing and assembling the final copy.

3 محطة طاقة تجاربية عن طريق حرق النفايات TEMO-IPP

For more details, see [Kamareddine 2016] and TEMO-IPP Reports 2012-2014.

3.1 Filter of TEMO-IPP and their preparation for moving to Rayhaniyya Camp March/April 2018

290318TEMO-IPP_Demoplant_Filters.pdf N

4 وضع المنشأة التجاربية NLAP-WEDC في مخيم الاجئين في الريحانية وتشغيل المحطة

4.1 Project Planning

19March18NLAP-IncineratorProject_Rihan

4.2 Contract with URDA

مذكرة تفاهم MOU

الطرف الاول:AECENAR
الطرف الثاني:مخيم الريحانية عبر جمعية URDA

<u>البنود</u>:

1- المحافظة على السرية confidentiality

2- تعهد AECENAR بتدريب عدد من العمال (يحدد لاحقا) Training

3- تعهد URDA ب مساعدتنا (الاجتماعات، الاشغال)

4- تضع URDA بتصرفنا database عن المخيم (عدد الخيم، السكان،نوعية النفايات. .)

5- مساهمة URDA في الإعداد للمشروع (دراسة جيولوجية للأرض، تمهيدها، جدار دعم)

6- تتكفل AECENAR بدفع :

- مصاريف العمال (خلال الفترة التجريبية 3 اشهر)
- التشغيل (أدوات، أجهزة، تلحيم..)

7- تأمين الكهرباء لتشغيل المحطة من URDA

8- تأمين التمديدات الكهربائية لنقل الكهرباء بعد المولد من قبل URDA

9- تأمين مصدر ماء من داخل المخيم من قبل URDA

10- بناء سور حول المحطة من قبل URDA

11- لا تتحمل AECENAR مسؤولية في حال حدوث أية حادث

12- المساهمة في عملية الفرز (الجمع، الحاويات)

13- تأمين إذن دائم (الدخول والخروج) ومكان للسيارة

14- في حال حدوث أي طارئ ، يرجى تبليغ:

- المسؤول في AECENAR
- الإسعاف
- الدفاع المدني
- تأمين لائحة أرقام الطوارئ

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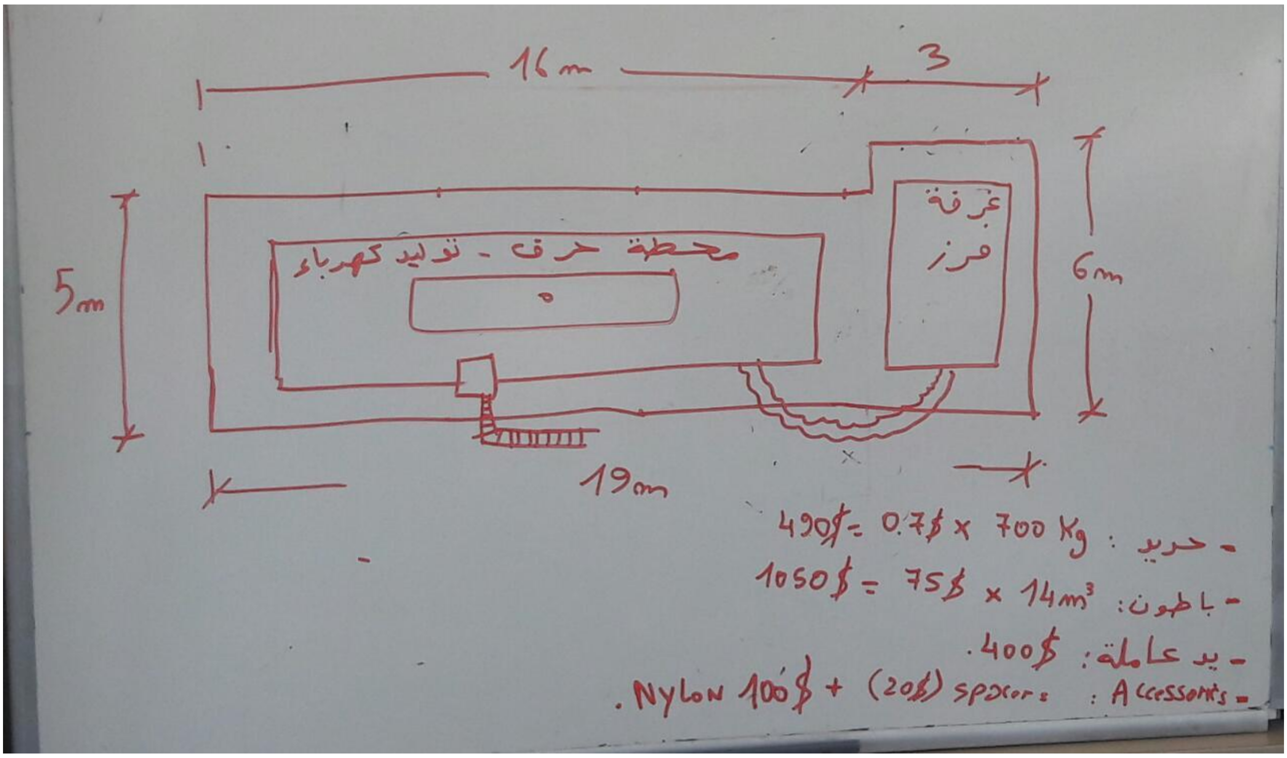
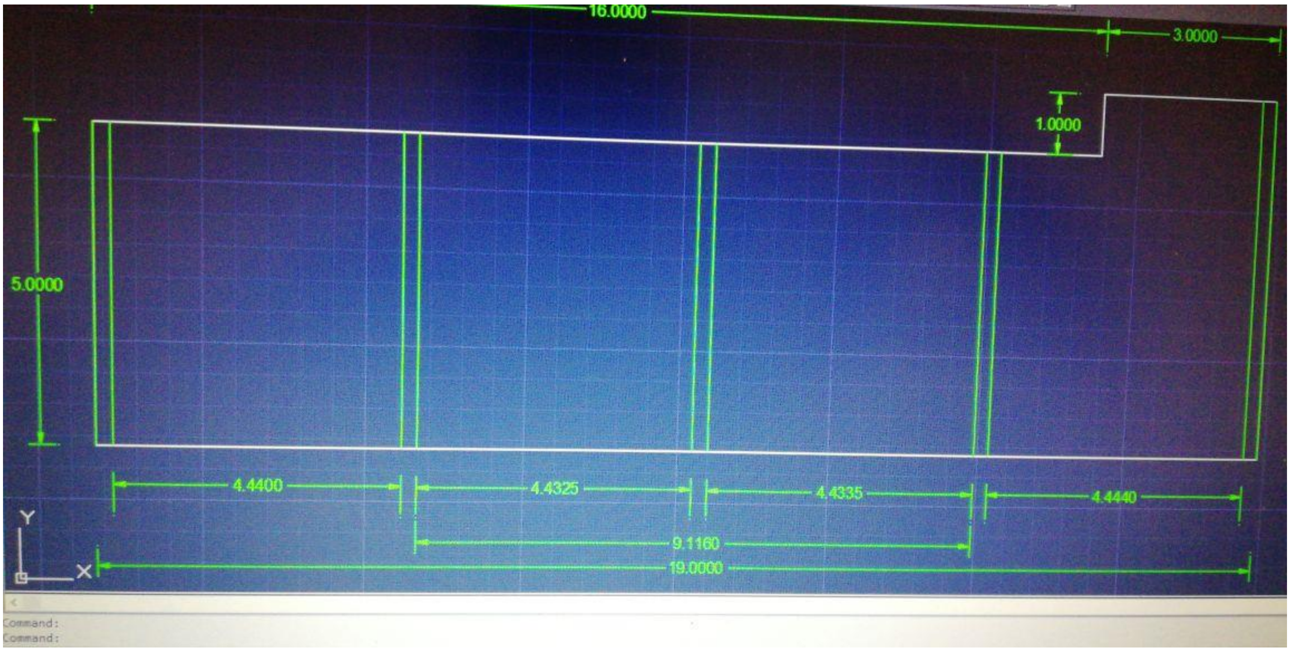
4.3 Ground Planimetry



- حديد : 490$ = 0.7$ x 700 Kg
- باطون : 1050$ = 75$ x 14m³
- يد عاملة : 400$.
- Accessoires : Nylon 100$ + (20$) spacer.



4.4 لمرحلة الأولى : AECENAR جرف الأرضية وتجهيزها للصب 18-4-2018

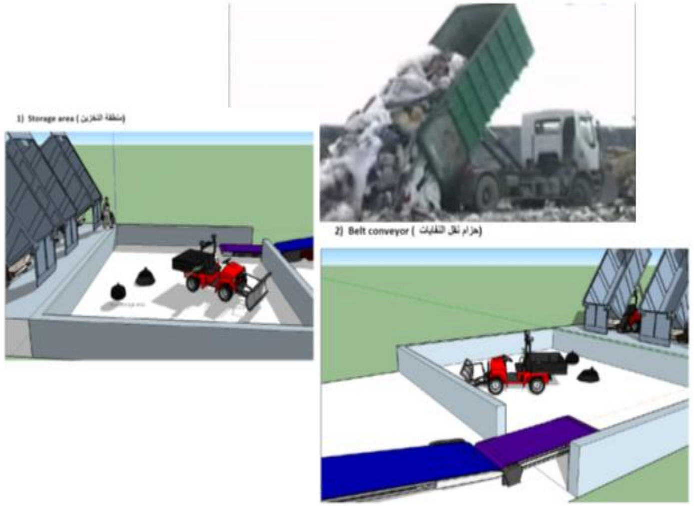
في مخيم الاجئين في الريحانية وتشغيل المحطة NLAP-WEDC **وضع المنشأة التجاربية**

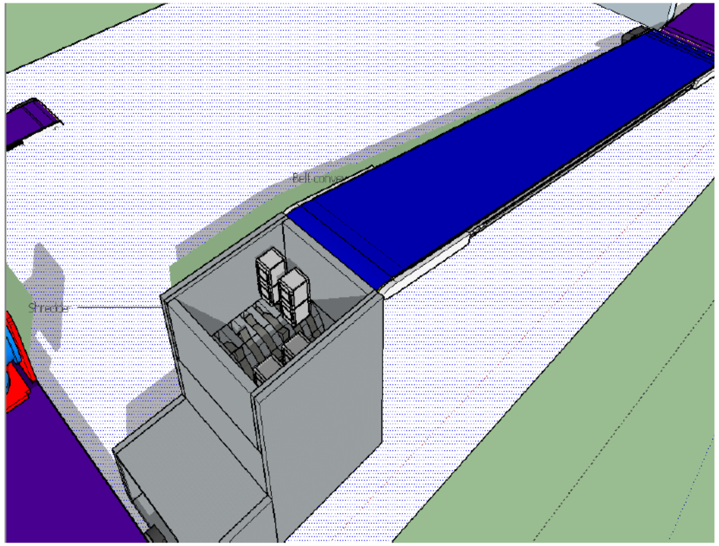
في مخيم الاجئين في الريحانية وتشغيل المحطة NLAP-WEDC **وضع المنشأة التجاربية**

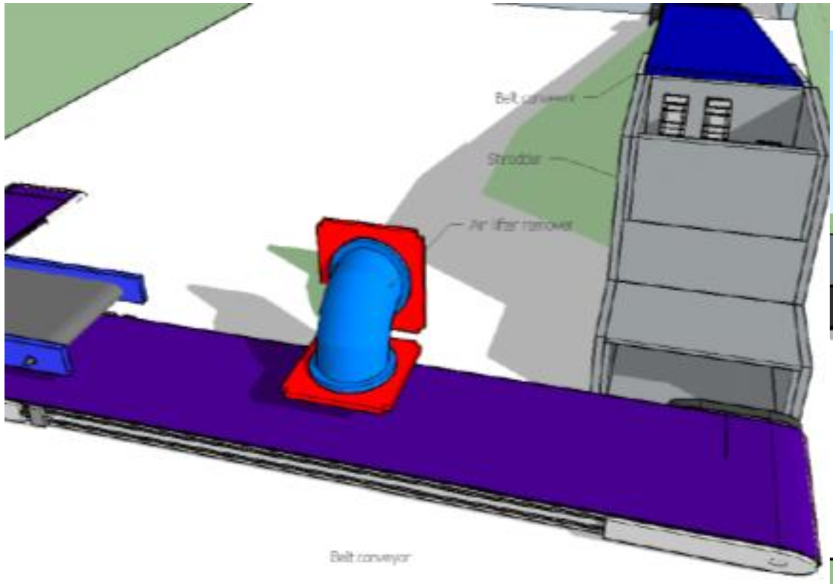
في مخيم الاجئين في الريحانية وتشغيل المحطة NLAP-WEDC **وضع المنشأة التجاربية**

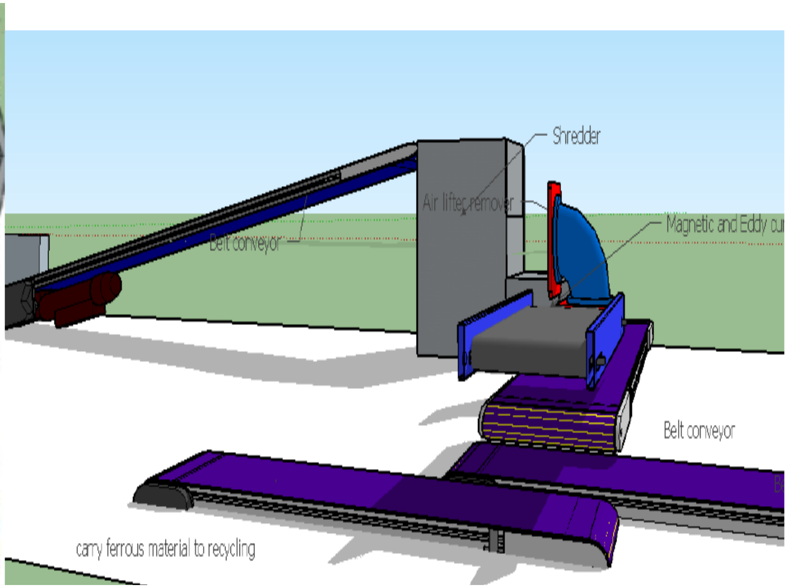
في مخيم الاجئين في الريحانية وتشغيل المحطة NLAP-WEDC **وضع المنشأة التجاربية**

5 Waste input Unit









6 Bioethanol/Distillated water (DW) production Unit

The concept is to produce pure distillated water (e.g. for medical laboratories) using the outlet steam at the turbine exit. Instead of simply going to the condensor, the outlet steam of TEMO-IPP 40kW plant (110°C, 1,1 bar) and the condensor is used to distillate water from the cooling cycle.

The input to the process is the bioEthanol/water mixture from processed organic waste and sugar beet.

6.1 The series -cascade distillation train

This is a continuous distillation carried out in a train of six columns. This distillation train comprises a rectifying section wherein the concentration of salt is reduced from feed composition (3% bioEthanol) to overhead composition (about 1 %) and a stripping section wherein the concentration is increased from feed to tails composition (about 50% Ethanol). This still train operates at reduced pressures to take advantage of the higher volatility of water at low pressure.

These 6 columns are arranged in a series cascade of 4 stages, 2 columns each comprising the first and second stage, and single smaller columns in the third and fourth stages.

All stages are in series, with transfer of Ethanol/water mixture from stage to stage accomplished by returning all condensate from a higher stage to a plate near the bottom of the next lower stage. A stream of liquid from the base of the lower stage equal to the amount of this condensate plus the product draw-off is sent forward to the higher stage. Several feed points are provided in the first stage so that the feed concentration can be matched to the operating column concentration.

6.2 Equipment description

Stage No.	**#columns in the stage**	**Diameter**	**Height**	**Number of plates**[13]	**Nominal holdup**[14] **gallons (تنكة)**	**Reboiler area**	**Condenser area**
1	2	0.32m (12 inch) 0.24m (10 inch)	2.47m 2.74m	7 8	5.8 4.5	0.6967 m^2	5.574 m^2
2	2	0.32m (12 inch) 0.24m (10 inch)	2.47m 2.74m	7 8	5.2 4.5	0.6967 m^2	5.574 m^2
3	1	0.17 m (6 inch)	2.35m	7	1.6	0.1858 m^2	1.4864m^2
4	1	0.08 m (3 inch)	2.35m	7	0.35	0.4645 m^2	0.3716m^2

Table 5: Equipment Description 1:10 length, 1:100 areas, volumes 1:1000

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[13] plate spacing in all columns is 12 inches

[14] holdup includes associated calandria and /or condenser

Bioethanol/Distillated water (DW) production Unit

In addition to this equipment, each stage is equipped with two stage steam jet eductors which operate off the condenser head space to maintain system vacuum. All gases reaching the jets first pass through ammonia refrigeration units which recover essentially all of the water vapor.

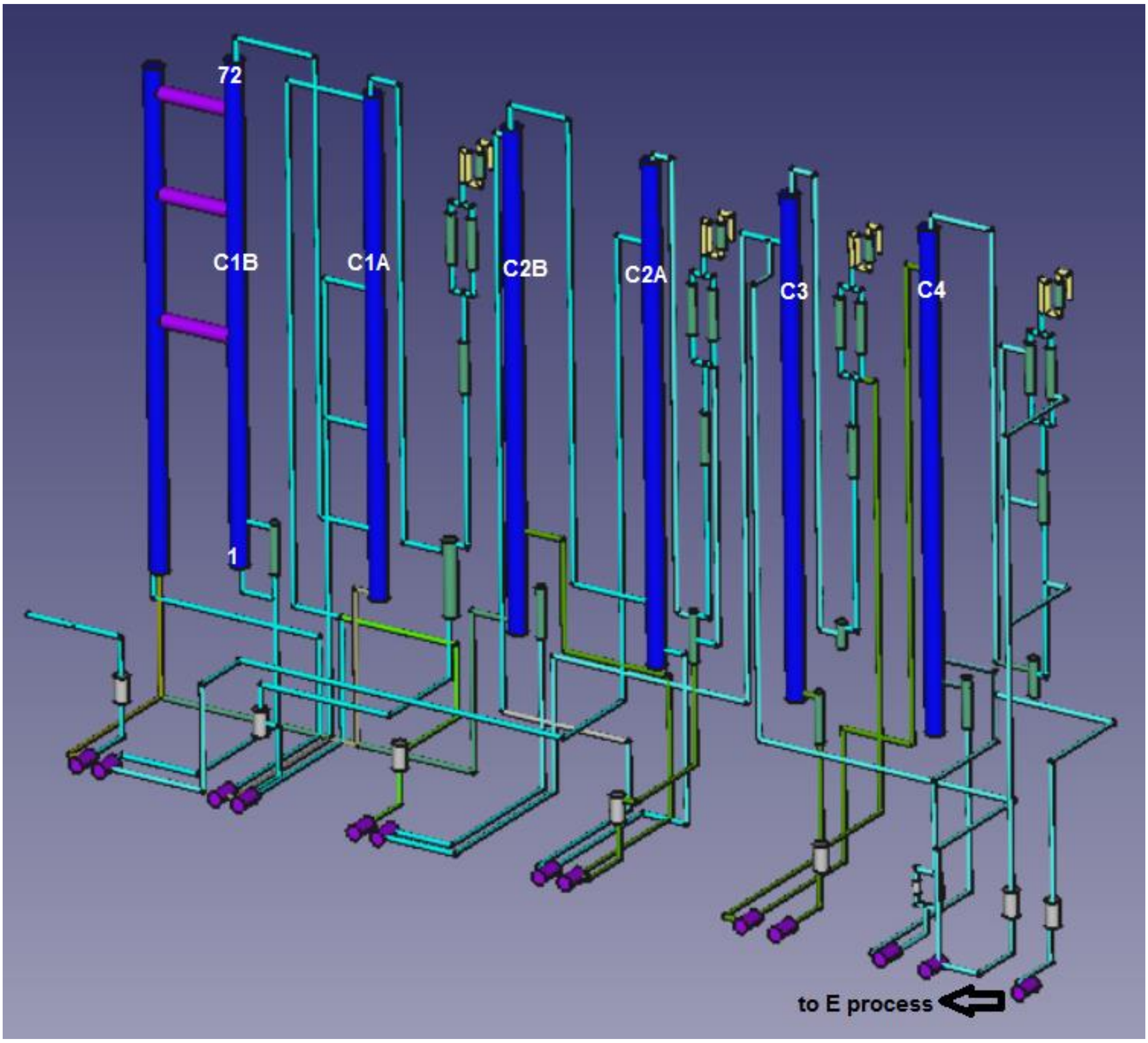

figure 7: capture of DW unit

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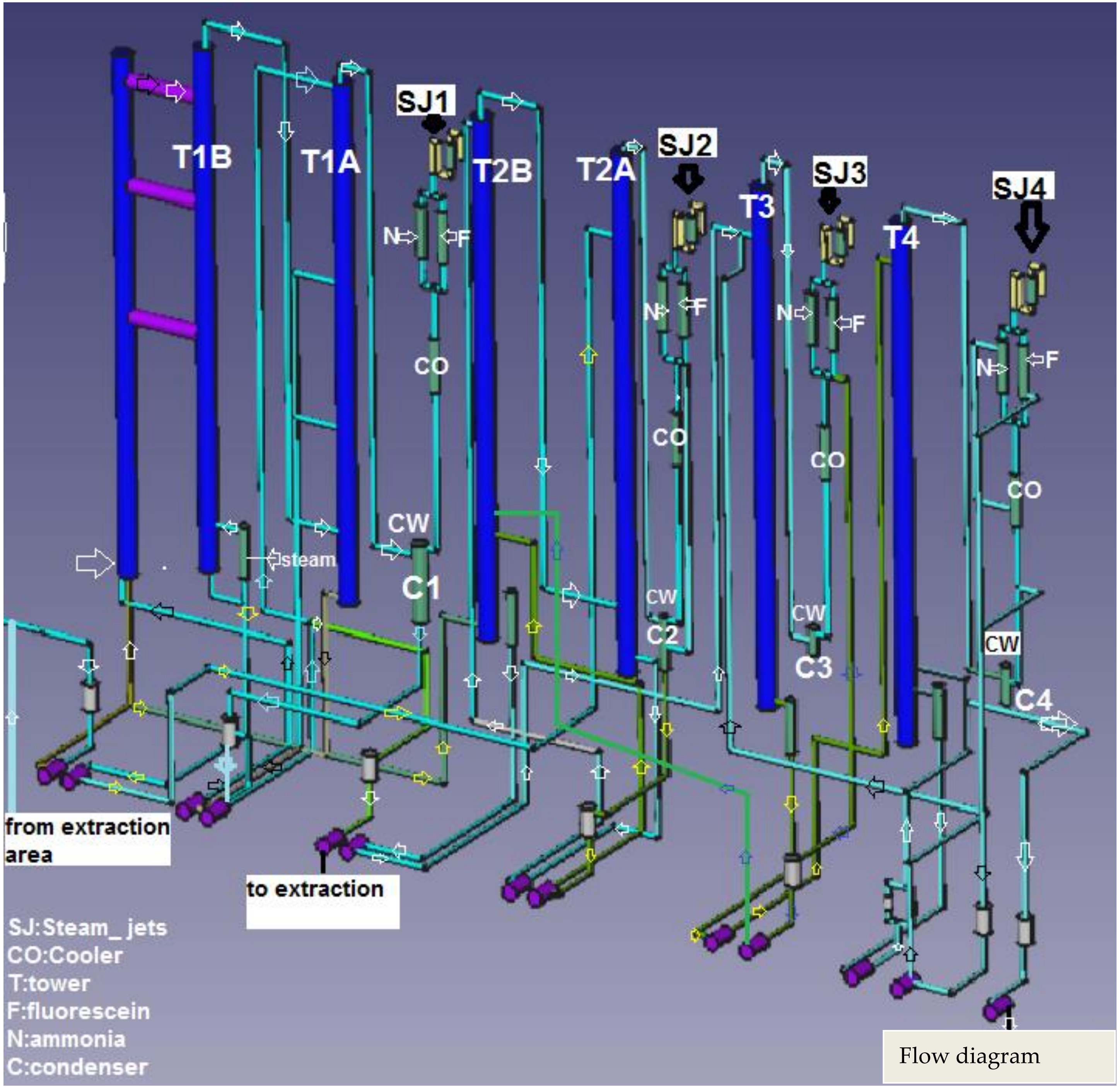
Bioethanol/Distillated water (DW) production Unit



6.3 Fundamental principles of DW plant design

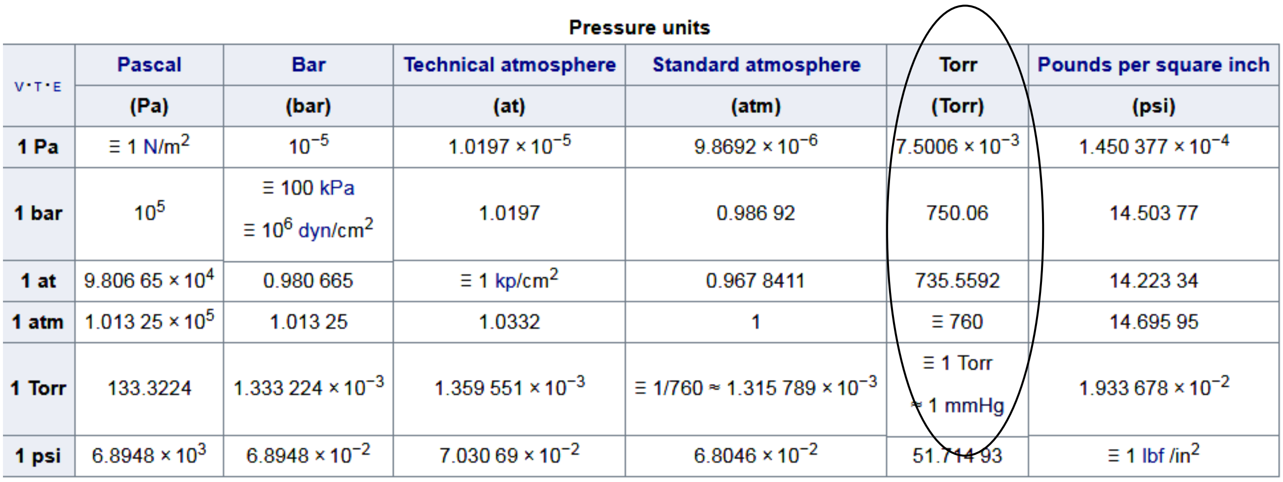
6.3.1 Relative volatility

The relative volatility of the water and Ethanol varies with temperature, and with the pressure prevailing in the distillation equipment.

6.3.2 Operating pressure

The lower the pressure at which the distillation process is operated, the greater is the relative volatility, and consequently the smaller is the quantity of heat or the fewer the plates required for a given separation.

The preferred operation pressure for a DW column is 0,113 - 0,126 bar.



Pressure units

V·T·E	Pascal	Bar	Technical atmosphere	Standard atmosphere	Torr	Pounds per square inch
	(Pa)	(bar)	(at)	(atm)	(Torr)	(psi)
1 Pa	≡ 1 N/m^2	10^{-5}	1.0197×10^{-5}	9.8692×10^{-6}	7.5006×10^{-3}	$1.450\,377 \times 10^{-4}$
1 bar	10^5	≡ 100 kPa ≡ 10^6 dyn/cm^2	1.0197	0.986 92	750.06	14.503 77
1 at	$9.806\,65 \times 10^4$	0.980 665	≡ 1 kp/cm^2	0.967 8411	735.5592	14.223 34
1 atm	$1.013\,25 \times 10^5$	1.013 25	1.0332	1	≡ 760	14.695 95
1 Torr	133.3224	$1.333\,224 \times 10^{-3}$	$1.359\,551 \times 10^{-3}$	≡ 1/760 ≈ $1.315\,789 \times 10^{-3}$	≡ 1 Torr ≈ 1 mmHg	$1.933\,678 \times 10^{-2}$
1 psi	6.8948×10^3	6.8948×10^{-2}	$7.030\,69 \times 10^{-2}$	6.8046×10^{-2}	51.714 93	≡ 1 lbf /in^2

Practical consideration of this equipment, preclude the use of pressures much below 130 mbar, at the top plate of column. the more important are the pressure drop in the condenser system and the pressure drop across each plate of the column itself.

* a pressure drop of 3.5 mm Hg per plate at the vapor rate given in next point

** a vapor _carrying capacity of 122.47 kg/hr*ft*ft of column cross sectional area at 100 mm Hg absolute pressure.

6.3.3 Flexibility of the DW process

An important characteristic of the DW is the fact that as the throughput of Ethanol is reduced, the train is able to handle a lower feed concentration. Since the E process can also handle lower feed compositions at lower throughput rates, this weaker than design material was taken into the E plant and concentrated to full strength. This flexibility is important for two reasons:

1. It is not necessary to achieve design concentrations in pre-dw unit in order to obtain some production of Ethanol.

2. by holding low concentrations in the DW train at reduced throughput the amount of Ethanol held up in the train is lower.

6.4 Process control

6.4.1 General principles

The DW plant is relatively simple to operate. As is the case with any continuous distillation process, flow control is of primary importance, and the more uniformly the various critical flows are maintained the better will be the performance of the still train. The critical flows are

1- steam to each reboiler

2- flow of liquid pumped from base of each tower to next tower in series

3- pre-DW product fed to still training

4- overhead product withdrawn from still train for return to pre-DW

The problem of operating the DW train is essentially one of balancing flows to and from each tower so that the liquid level in each stays within permissible limits. Because of the characteristics of the system it has proved simpler to do this by flow controllers rather than by level controllers. This means flows are held constant and levels are allowed to drift slightly to compensate for minor deviations from perfect balance. Slight corrections to flow settings are made as necessary to fold levels within bounds.

A discussion of still train operation logically starts with steam flow. Each column is capable of carrying a certain vapor load and to bring about this vaporization there is required a definite quantity of steam at the reboiler. The first flows shall be fixed, therefore are the steam flows.

6.4.2 Process

> The first stage consists of 2 towers connected to operate as a single column. All liquid which flows down one tower is pumped from the base of that tower to the top of the second tower, and all vapor leaving the top of the second passes to the base of the first tower.

> to start the first stage, sufficient feed is admitted to fill the plates and the reboiler, cooling water flow is established through the condenser, steam is turned on and established at the standard flow for this stage, and all of the condensate from the condenser is allowed to return to the top plate(total reflux).

>feed is then started at an appropriate rate. The same time a flow of overhead draw-off is started from the condenser in amount equal to the feed.

> to determine whether overhead draw-off rate is exactly equal to the feed rate, it is only necessary to observe the trend of liquid level in the base of the column adjacent to the reboiler. The draw-off rate is then adjusted slightly to correct any drift observed in this liquid level. Thus the technique of operation consists in setting flows of steam and feed at predetermined values, setting flow of overhead draw-off equal to flow of feed, then making minor adjustments in the flow of overhead draw-off in order to make this flow balance exactly with the feed.

> the stage is now operating to concentrate Ethanol, and the Ethanol content of the material at the reboiler end of the stage will gradually increase.

> Now the second stage has been put into operation on total reflux in a manner similar to that described for the first stage. The two stages are then connected together by introducing the total flow of liquid from the second stage condenser into the second plate (counting from base) of the first stage, and at the same time pumping liquid at an equal rate from the base of the first stage to the top of the second stage. These two flows are balanced by observing the level in the base of the second stage and making minor adjustments in the flow of liquid entering the top of that stage. In a similar manner the remaining stages are successively placed in operation.

> in normal operation the total withdrawal of liquid from the train (first stage overhead plus final stage tails) must on the average equal the feed of liquid. The rate of draw-off from the base of the final stage however, is so small compared to the amount of liquid in the train that variations in this rate of draw-off do not affect, the problem of controlling the other stages. The withdrawal of product from the final stage can therefore be varied at the operators discretion, the base of the column acting, in effect, as a small, internal, holdup tank for product.

> if no product is withdrawn from the final stage, the concentration of Ethanol at the base of that stage will gradually increase toward a steady stage value. After withdrawal of product is started the Ethanol concentration will level out some lower value. The composition of the material withdrawn as product from the base of the final stage can be varied over a considerable range simply by varying the total amount withdrawn. As the rate is increased, the Ethanol. content falls, as the rate is reduced, the Ethanol content rises.

6.4.3 Operating pressure

The preferred range of operating pressure for a DW column is 85 to 95 mm Hg absolute, measured in the condenser vent line. The pressure drop through the vapor line and condenser is about 10 mm Hg so that the pressure above the top plate will be about 95 to 105 mm Hg. As previously noted, operation at a higher pressure will increase the productivity of the still train. This is so because the vapor carrying capacity of the still columns is directly proportional to the square root of the operating pressure. As the pressure is raised, the relative volatility decreases, and the steam consumption increases at a greater rate than does the productivity.

6.4.4 Boil-up rates

Column capacity is related to vapor density and vapor velocity by the following formula which has been developed as a design index of capacity has been found that operation at *F* factors much above 1 results in marked increases in plate to plate entrainment with consequent loss of plate efficiency.

$$F = \mu \sqrt{\rho}$$

where μ = vapor velocity, ft/sec (average velocity over column cross section)

ρ = vapor density, lb/ft^3

F = index of column capacity

at the design condition of 0,136 bar pressure the density of saturated water vapor is 0.1 g/m^3 by solving for u in the above equation, there is obtained a value of 4 m/s the vapor rate per square meter of area is then 1350 g per hour.

V=1:1000, A=1:100

6.4.5 Process losses

Only the bottom of the second column in the first stage, the process pumps and pump discharge lines operates at pressure above atmospheric.

Column head pressure	range	Normal
First stage		75 mbar
Second stage		75 mbar
Third stage		75 mbar
Third stage		75 mbar

Boilup rates	Maximum g/hr	Normal
First stage	15000	
Second stage	15000	
Third stage	4000	
Third stage	850	

Table 6: DW process standard operation conditions

Therefore there is very little hazard of product loss in the DW process. However, product dilution can occur through calandria or condenser tube leaks or through air in-leakage carrying with it natural concentration water vapor. Product dilution is controlled by periodic fluorescein dye injection on the calandria steam chests and condenser cooling water. Any dye concentration showing up in the process steam is indicative of a leak. Air in-leakage is detectable by the closing of a pressure controlling air bleed which is located in the steam suction. Closing of this valve and overload of the ammonia coolers both indicate that there is an air leak in the column which the jet and cooler are associated.

All tanks or equipment in the atmosphere pressure parts of the feed, tails or overhead systems where water vapor escape are protected bz passing all of the vents for such equipment through ammonia cooler or desiccant traps.

6.5 Construction Materials

Stage No.	**#columns in the stage**	**Diameter**	**Height**	**Number of plates[15]**	**Nominal holdup[16] gallons (تنكة)**	**Reboiler area**	**Condenser area**
1	2	0.32m (12 inch) 0.24m (10 inch)	2.47m 2.74m	7 8	5.8 4.5	0.6967 m^2	5.574 m^2
2	2	0.32m (12 inch) 0.24m (10 inch)	2.47m 2.74m	7 8	5.2 4.5	0.6967 m^2	5.574 m^2
3	1	0.17 m (6 inch)	2.35m	7	1.6	0.1858 m^2	1.4864m^2
4	1	0.08 m (3 inch)	2.35m	7	0.35	0.4645 m^2	0.3716m^2

Table 5: Equipment Description 1:10 length, 1:100 areas, volumes 1:1000

Stage	Numbers of columns	Column Manteau Surface [m^2]	Number of plates
1	2	2,8 2,2	7 8
2	2	2,8 2,2	7 8
3	1	1,30	7
4	1	0,57	7
Total		11,87	44

The columns are made of stainless steel type 304

6.5.1 Distillation Bubble caps plate

This the details of construction of such bubble cap plate

Metal Casting (صب المعادن): Ahmad +961 76361241 (Miniye)

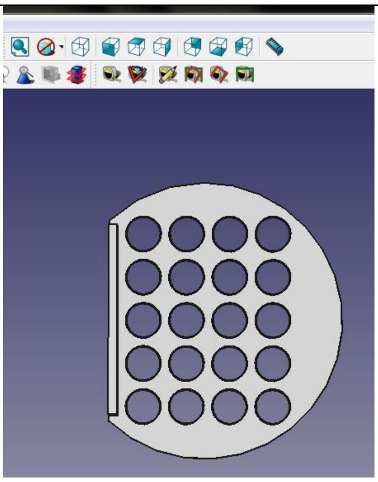
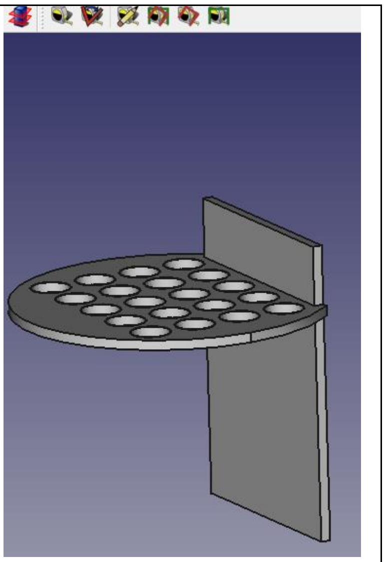
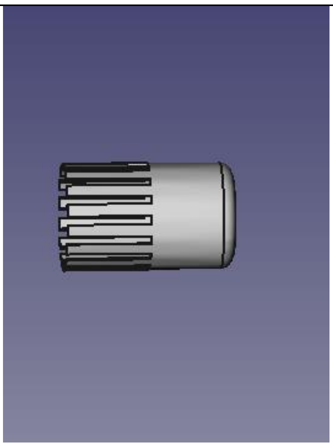
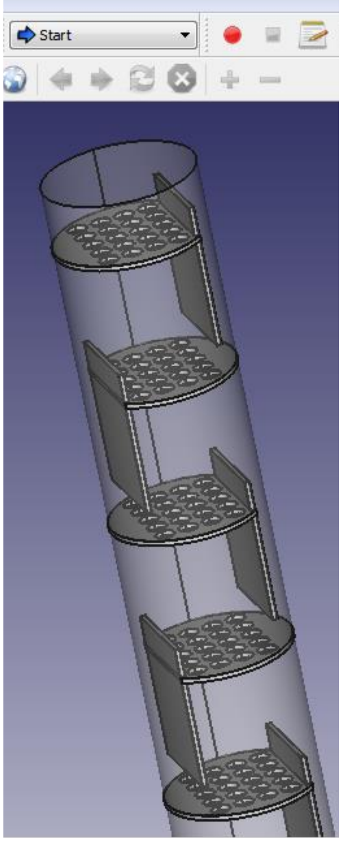
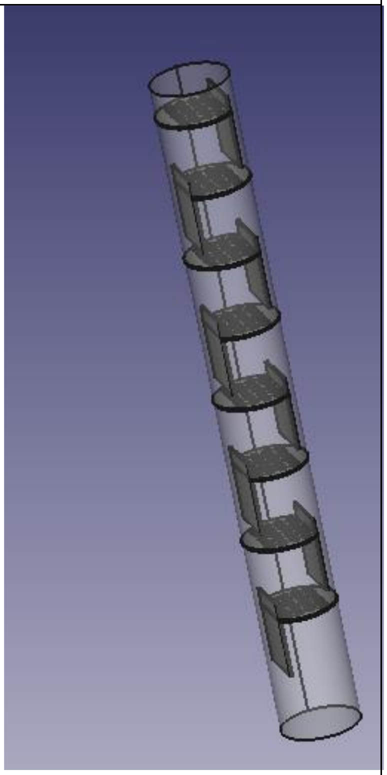
---

[15] plate spacing in all columns is 12 inches

[16] holdup includes associated calandria and /or condenser

Bioethanol/Distillated water (DW) production Unit

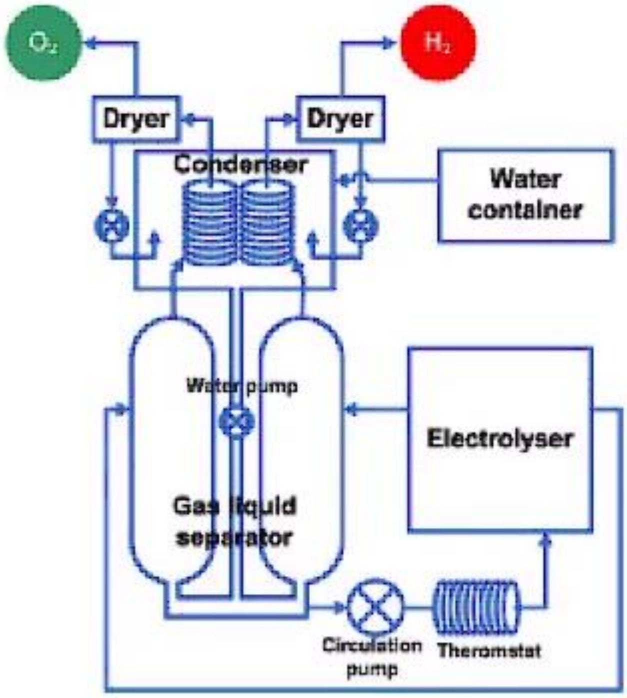
Bioethanol/Distillated water (DW) production Unit

OneBubble plate distillation040118.FCStd		
cap040118.FCStd		
bubble plate distillation040118.FCStd		

7 منظومة تحليل الكهربائي للماء (Electrolysis Unit)

7.1 Alkaline Electrolysis System Design from lightbridge.sales@gmail.com

Schematic of Alkaline Water Ele



Module of 2.5kW Electrolyser

Specification

Size:
52cm X 30cm X 50cm
Power Consumption:
<2.5kW
Gas production per hour:
hydrogen gas 500liter,
oxygen gas 250liter, separately
Pressure:
5 bar
Temperature:
50~80℃
Purity of gas:
hydrogen gas 99.9%,
oxygen gas 98%

Hydrogen valve open

Stainless steel cutting test

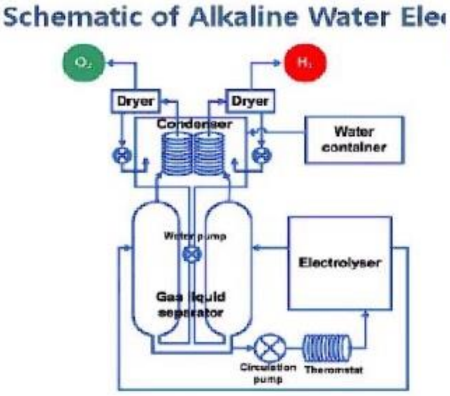
Module of 2.5kW Electrolyser

Specification

Size:
52cm X 30cm X 50cm
Power Consumption:
<2.5kW
Gas production per hour:
hydrogen gas 500liter,
oxygen gas 250liter, separately
Pressure:
5 bar
Temperature:
50~80℃
Purity of gas:
hydrogen gas 99.9%,
oxygen gas 98%

7.2 Tasks Project Plan

080318Tasks_NLAP-WEDC_ElectrolysisUnit_IncludingH2O2Storage.xlsx - 08.03.2018


Schematic of Alkaline Water Ele

Specification
Size:
52cm X 30cm X 50cm
Power Consumption:
<2.5kW
Gas production per hour:
hydrogen gas 500liter;
oxygen gas 250liter, separately
Pressure:
5 bar
Temperature:
50~80℃
Purity of gas:
hydrogen gas 99.9%,
oxygen gas 98%

NLAP-WEDC Electrolysis Unit /
Hydrogen and Oxigen Storage

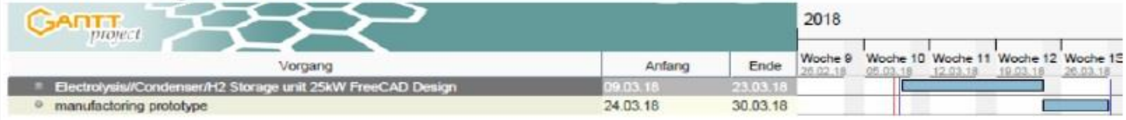
08.03.2018
http://

Project managers:	Samir
Dates:	09.03.2018 - 31.03.2018
Complete:	0%
Tasks:	2
People:	2

Tasks

Vorgang	Anfang	Ende
Electrolysis//Condenser/H2 Storage unit 25kW FreeCAD Design System FreeCAD Design - 25 kW Electrolysis Unit - Condensor (H2/O2 purification unit) - H2 Storage - O2 Storage (Each device in 1 file, the whole system in 1 file) Documentation: Piece List with prices	09.03.18	23.03.18
manufactoring prototype	24.03.18	30.03.18

Gantt-Diagramm



Vorgang	Anfang	Ende
Electrolysis//Condenser/H2 Storage unit 25kW FreeCAD Design	09.03.18	23.03.18
manufactoring prototype	24.03.18	30.03.18

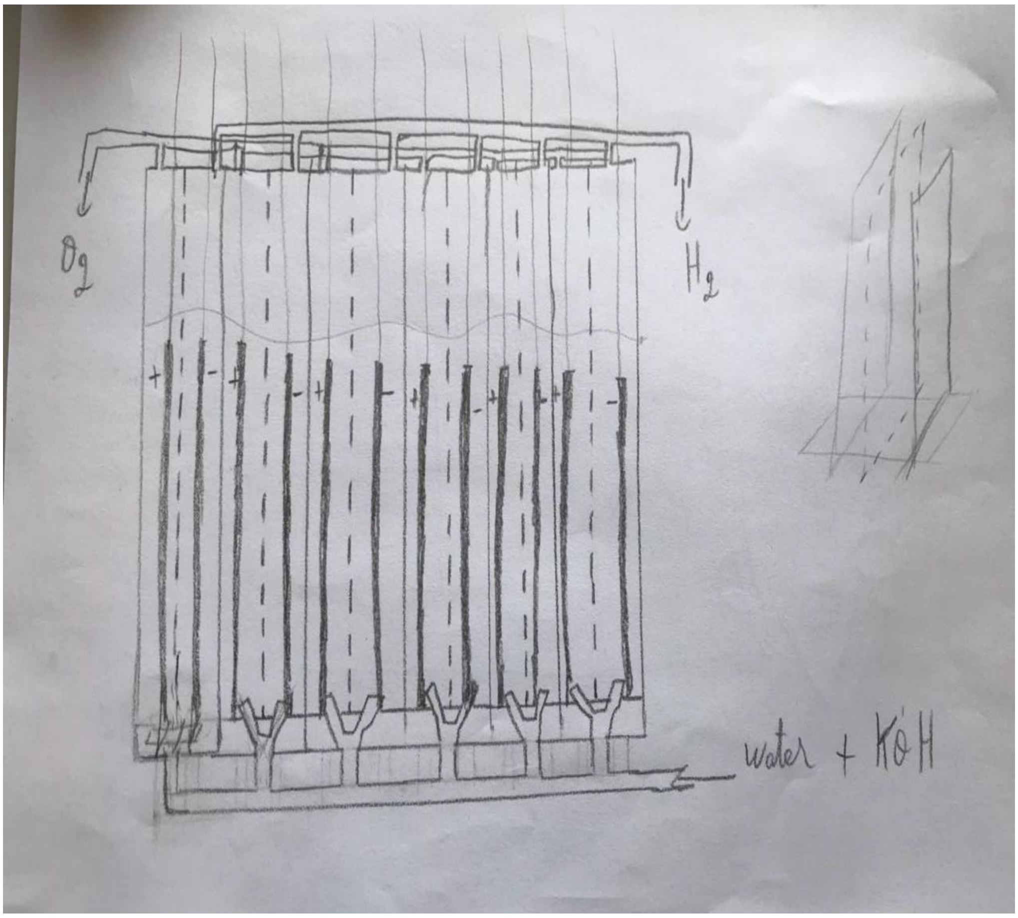
7.3 Prototype of electrolysis unit

7.3.1 Introduction

As part of the manufacture of alkaline electrolysis, it is necessary to make the proposed design of alkaline electrolysis then know the main materials to have a perfect electrolysis alkaline.

7.3.2 Design of electrolysis stack

7.3.2.1 Concept

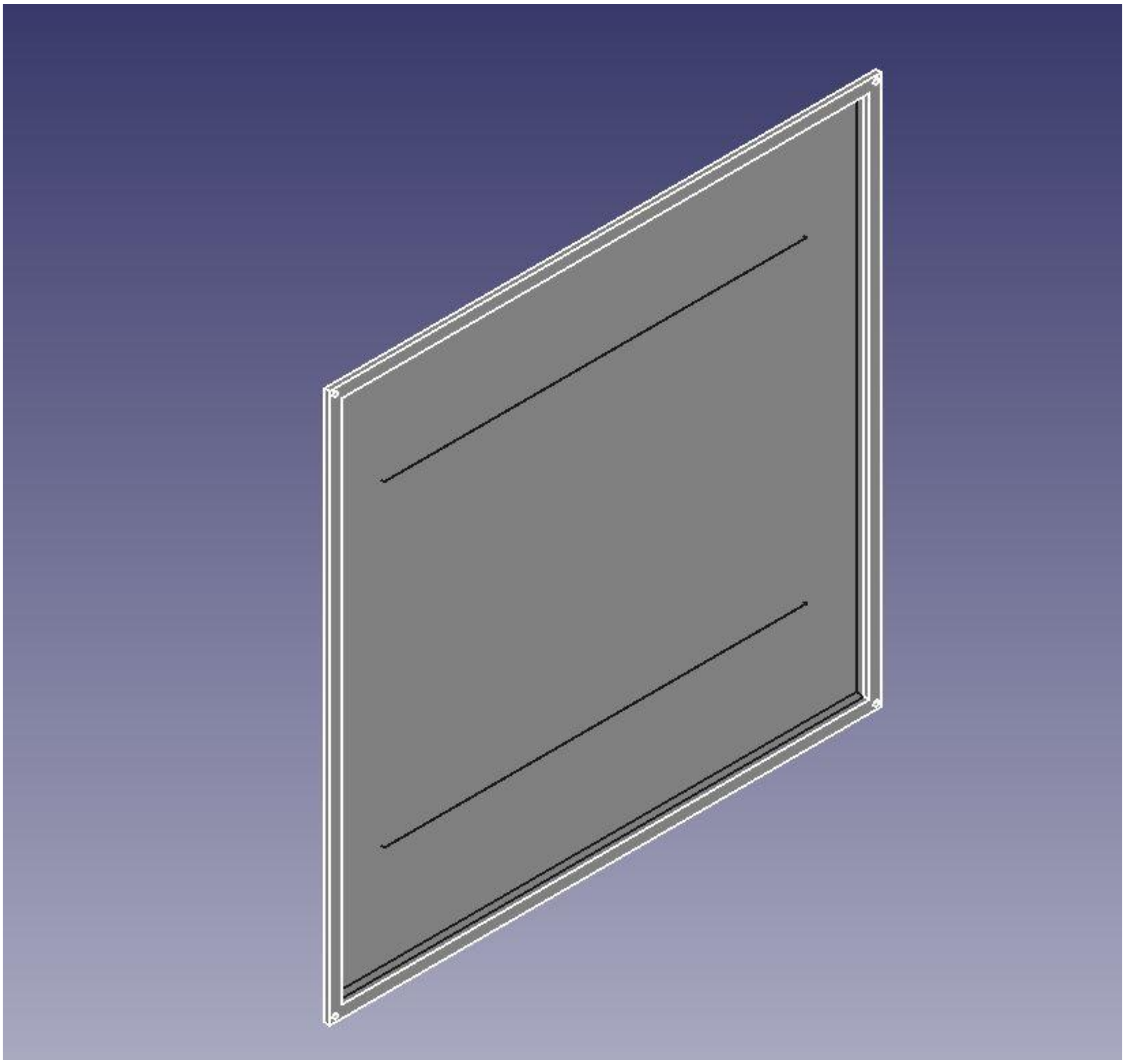


7.3.2.2 Design 1 (April 2018)

Electrolyse_cadre.FCStd

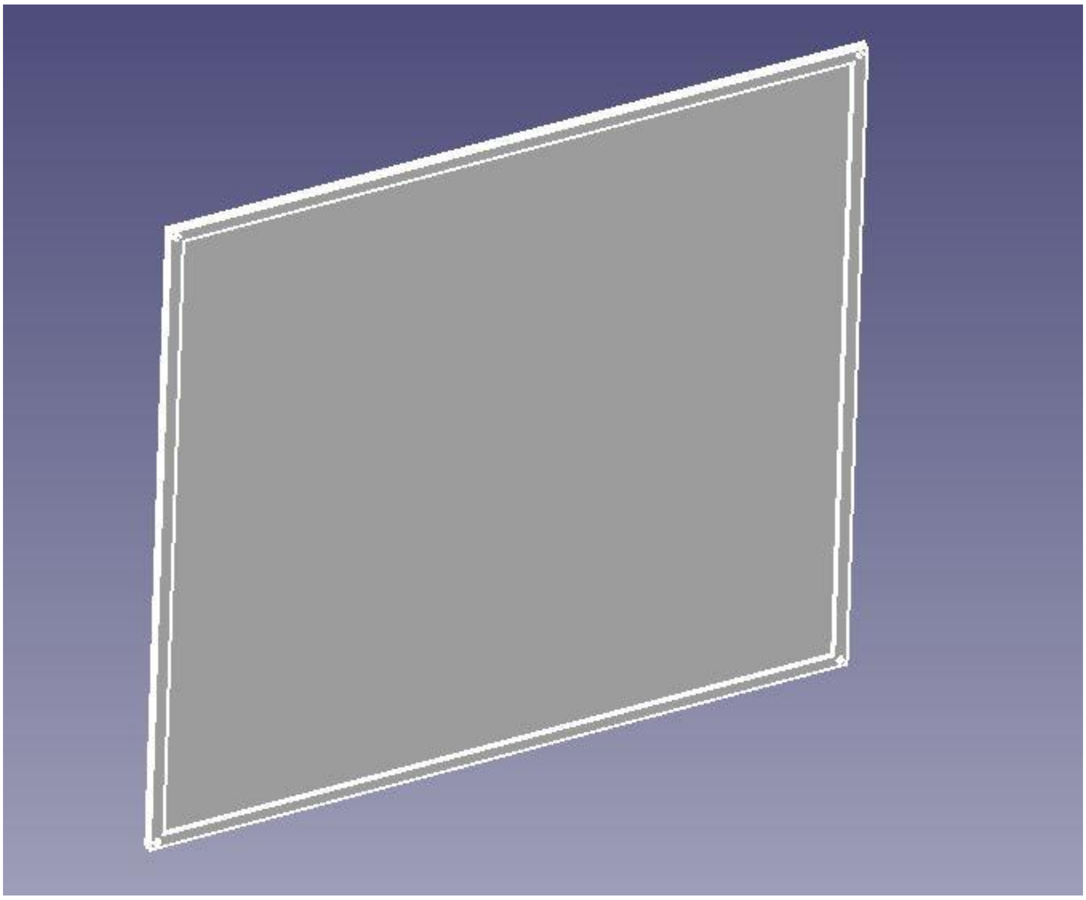
21042018_assemblage_electrolysis(color).F

Base plate for anode and cathode



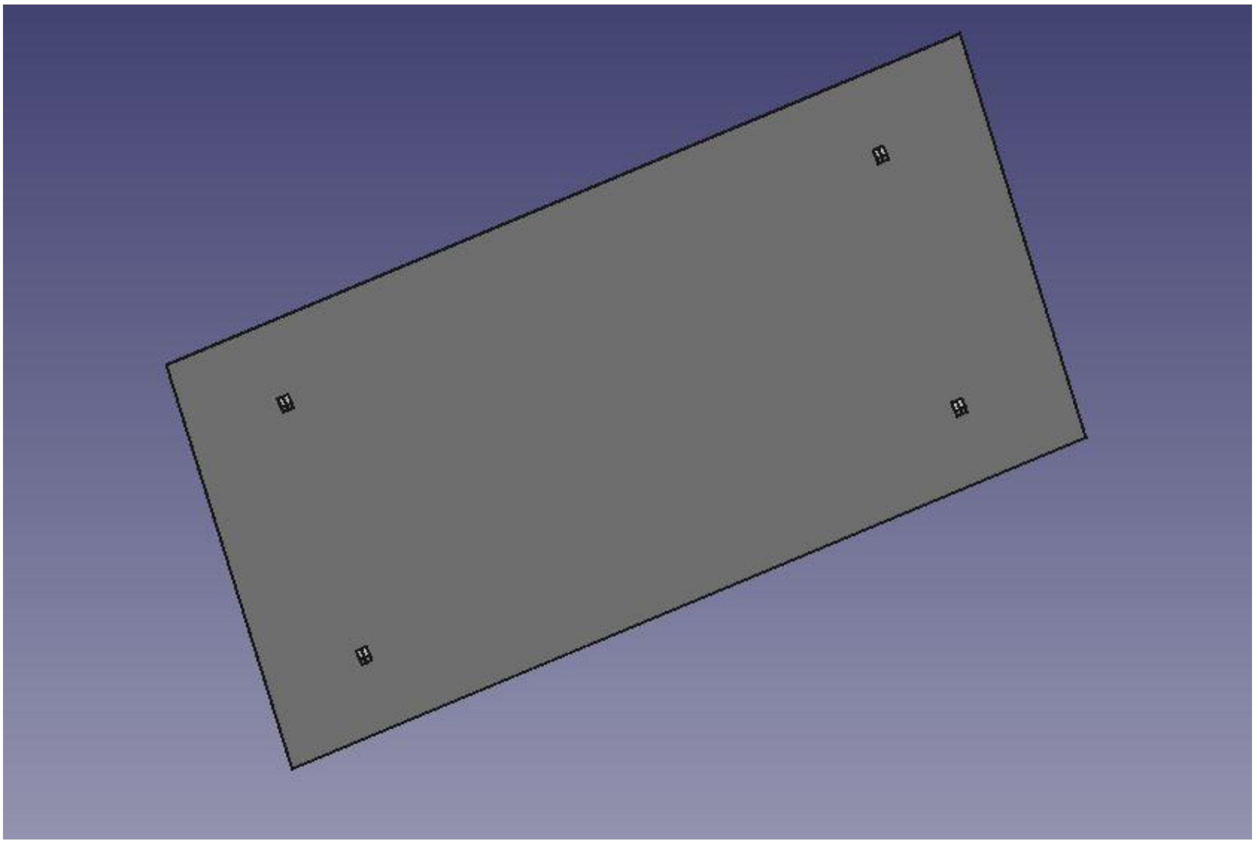
17042018_Prototype electrolysis.FCStd

Diaphragm



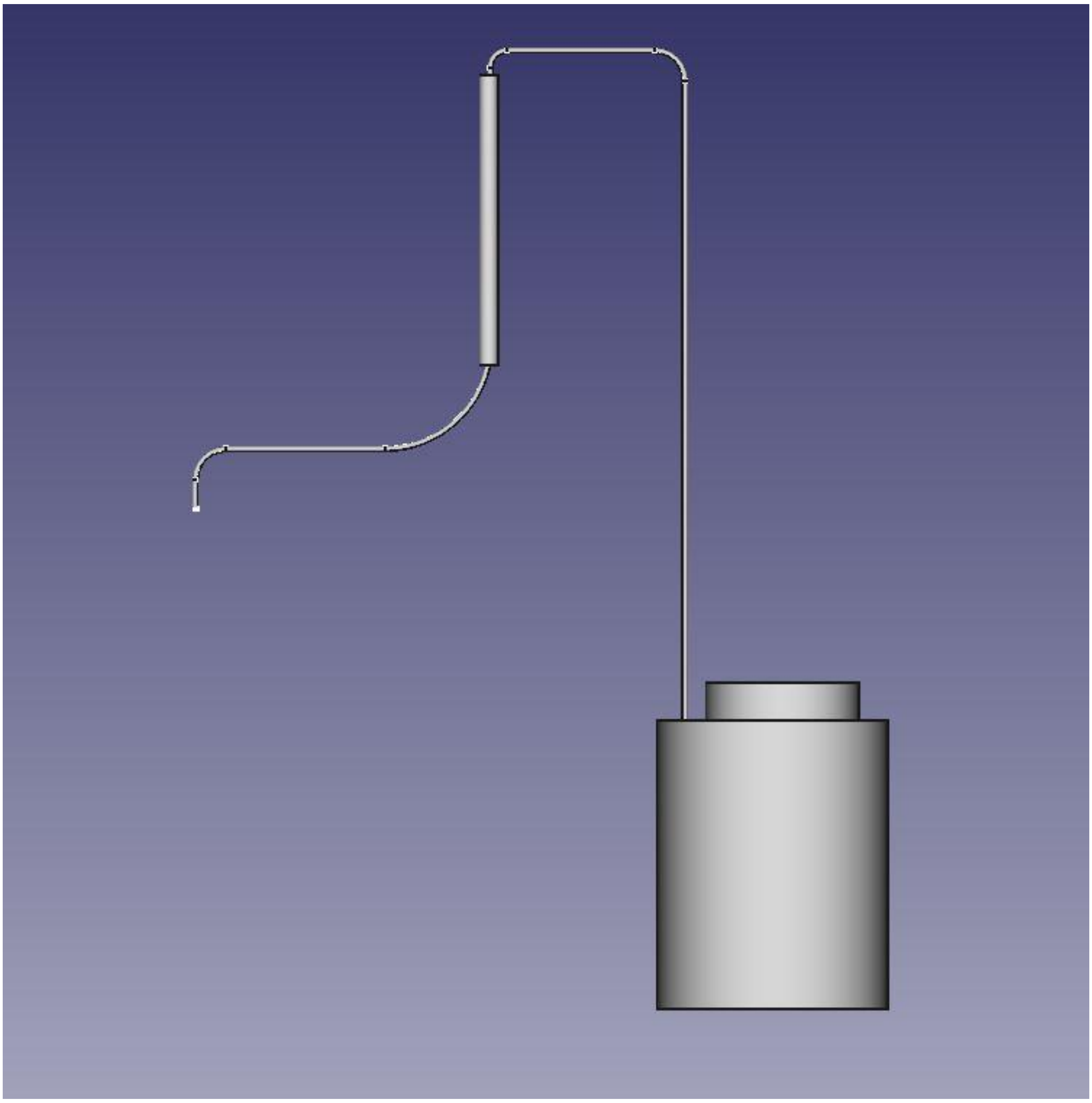
19042018_diaphragm
.FCStd

Electrode



19042018_electrode.FCStd

Pipe

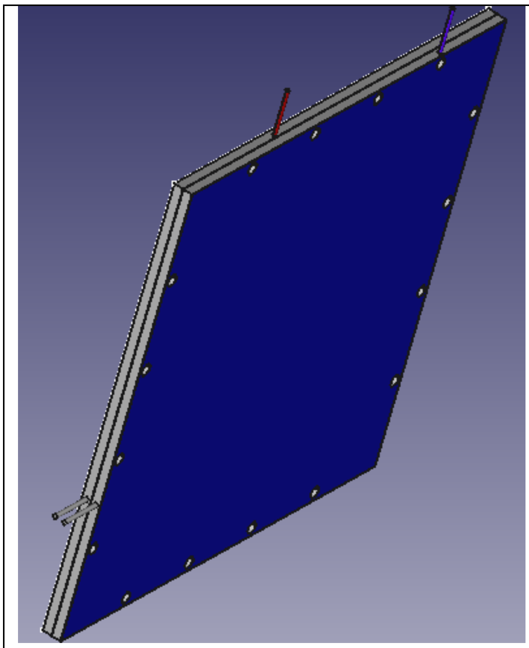


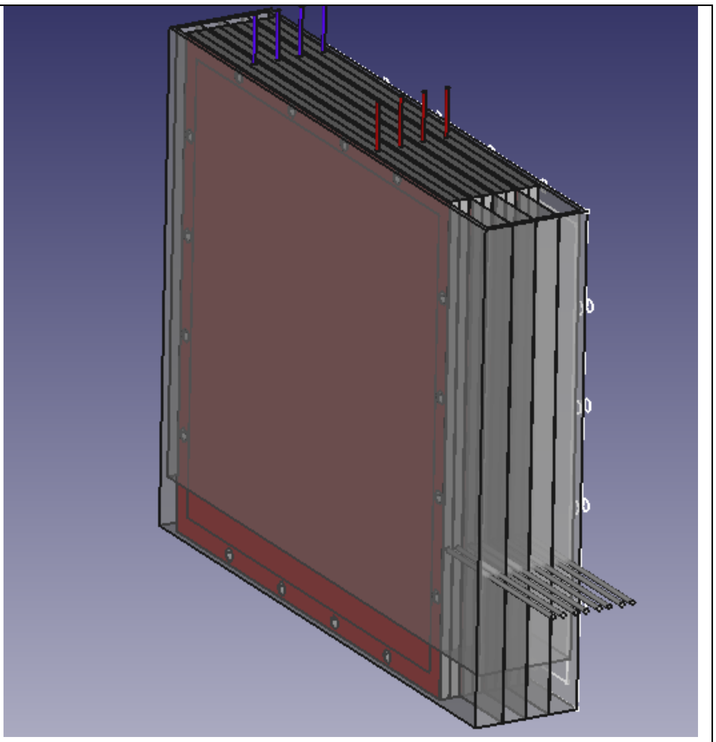
28042018_pipe.FCStd

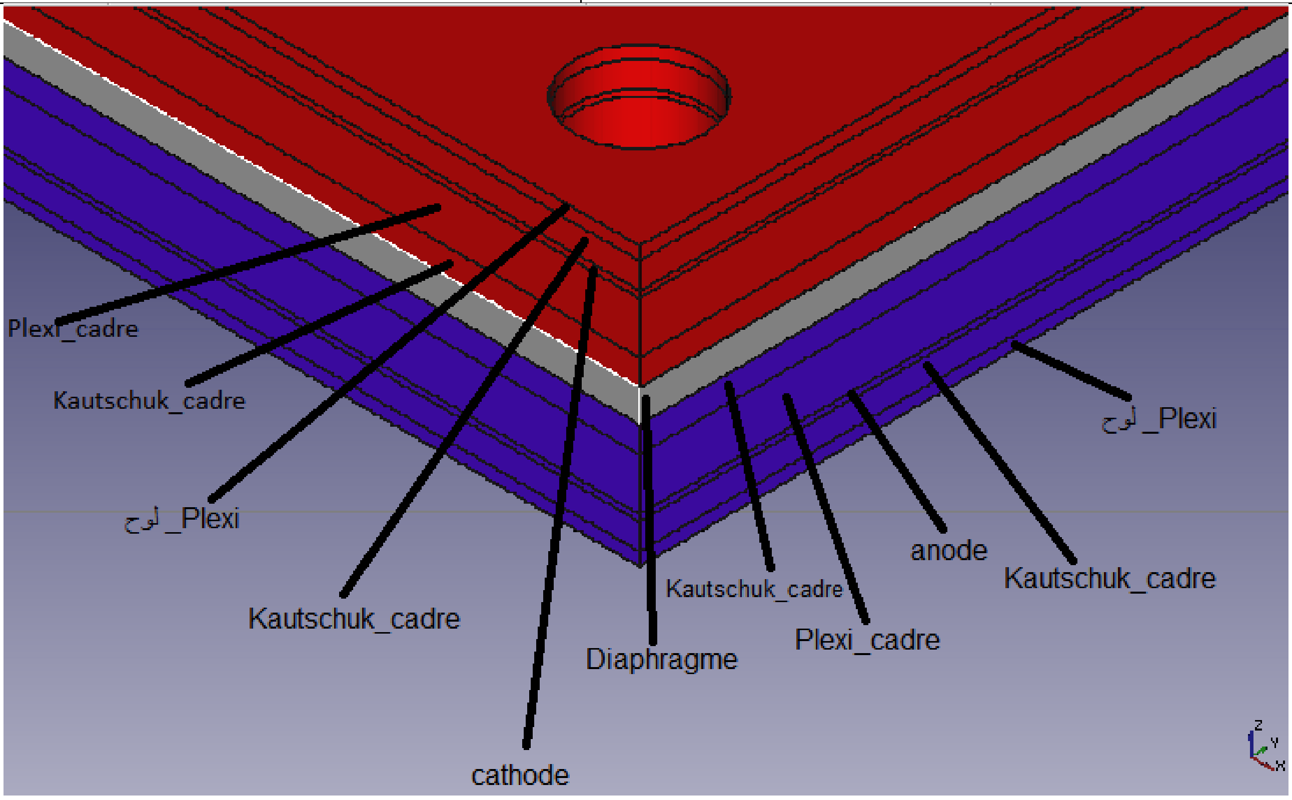
7.3.2.3 Design 2 (May 2018)

03052018_one_cell.FCStd	03052018_Stack_electr.FCStd

منظومة تحليل الكهربائي للماء (Electrolysis Unit)



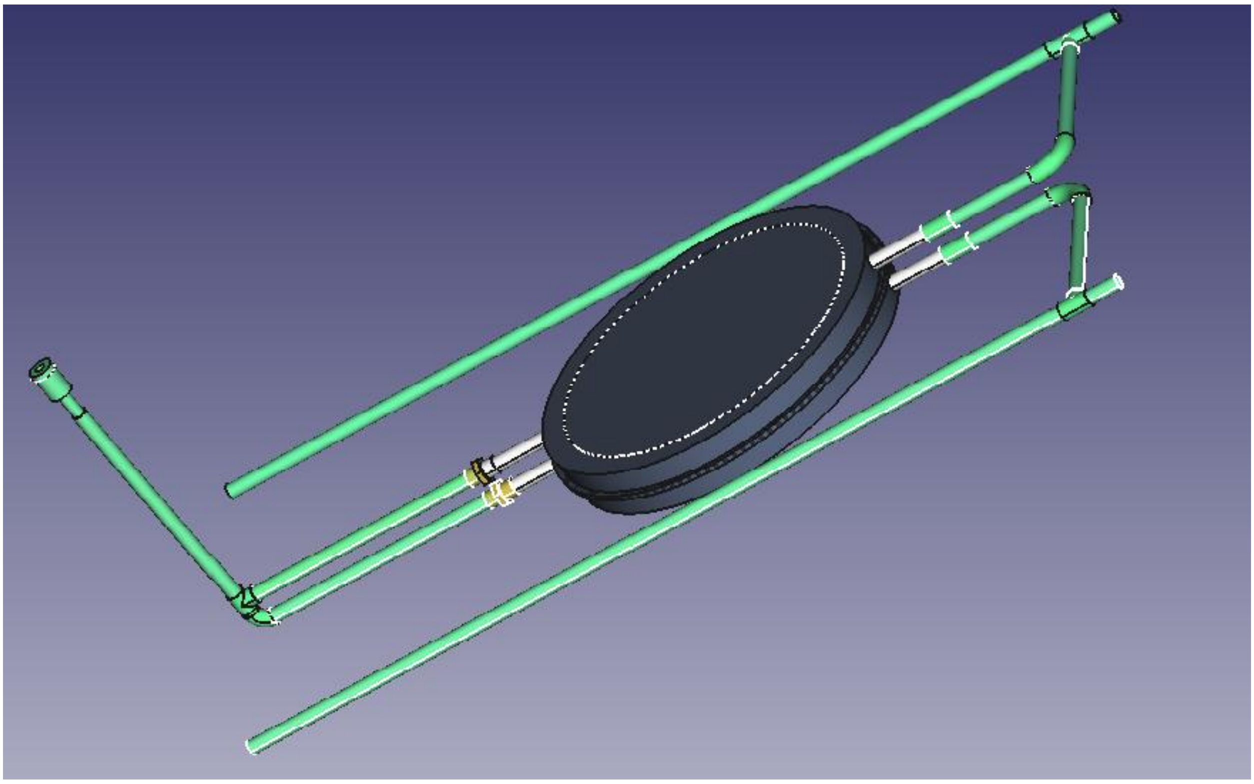




Result:

Plexi breaks, when two plates are pressed together such that the water can't flow out.

7.3.2.4 Design 3 (Aug 2018)



electrolyser 210818.FCStd

ELECTROLYSER:

A HYDROLIC MACHINE THAT SERT TO SEPARATE THE H2 FROM USUAL WATER (H2O) DURING THE SEPERATION PROCESS IT ALSO CONDUCT PURE WATER AS IT'S WASTE

LET'S GET OVER THE STEPS:

1-2 stainless plates tied up tightly

2- ppr pipes allowing the gas to flow freely

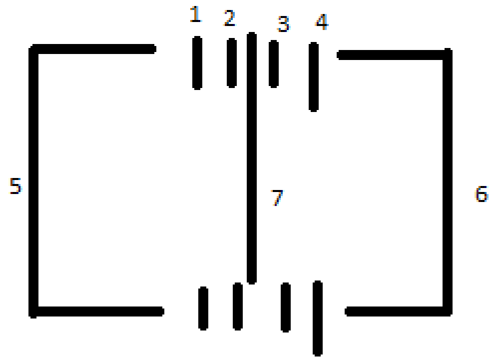
3- a plastic headed bound to prevent electrical contact between the 2 plates

4-retatchebel iron link to separate the 2 basic compounds [pipes,plates] (قطع وصل).

a NON-REVERSE LINK to prevent the water from turning back once it has been pumped .

The motor has initially the basic role to pump the water threw the device starting the mechanicsm witch whom it is meant for.

منظومة تحليل الكهربائي للماء (Electrolysis Unit)



1-industriel rolls

2-جلدة

3-جلدة

4-industriel rolls

5- stainless cathode

6-stainless anode

7- nafion membrain

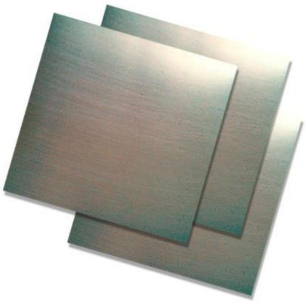
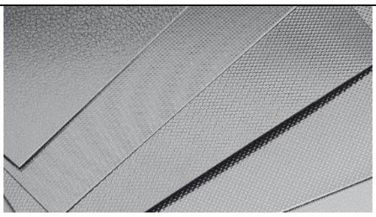
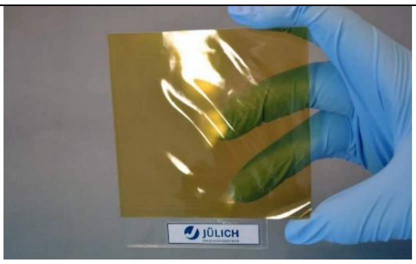
We have replaced the motor to a more accurate full-mechanic system , using relatively a small volume tank decreasing the water pressure in the pipes making a more efficient and accurate mechanicsm

7.3.3 Materials

2 plates plastic	1m * 1m
8 plates plastic	1.1 cm * 1m
4 plates caoutchouc	1m * 1m * 0.5 cm
1 plate Stainless	95 cm * 90 cm
1 plate Nickel	95 cm * 90 cm
2 tubes Nickel	Φ 1cm L:10 cm
2 tubes Stainless	Φ 1cm L:10 cm
6 tubes plastic	Φ 2cm L:10 cm
7 tubes plastic	Φ 2cm L:20 cm

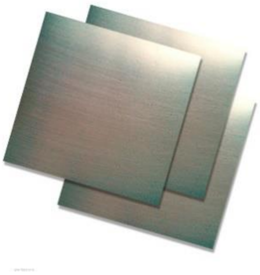
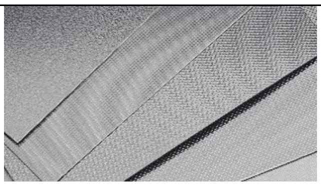
منظومة تحليل الكهربائي للماء (Electrolysis Unit)

7 elbows plastic	Φ 2cm ╔
2 tubes plastic	Φ 2cm L: 1m
2 T plastic	Φ 2cm ╣
2 condenser	
2 faucet	
2 tank plastic	
2 fixes bolt	

Electrolyte (KOH)	
Anode (Nickel)	
Cathode (Stainless)	
Diaphragm	

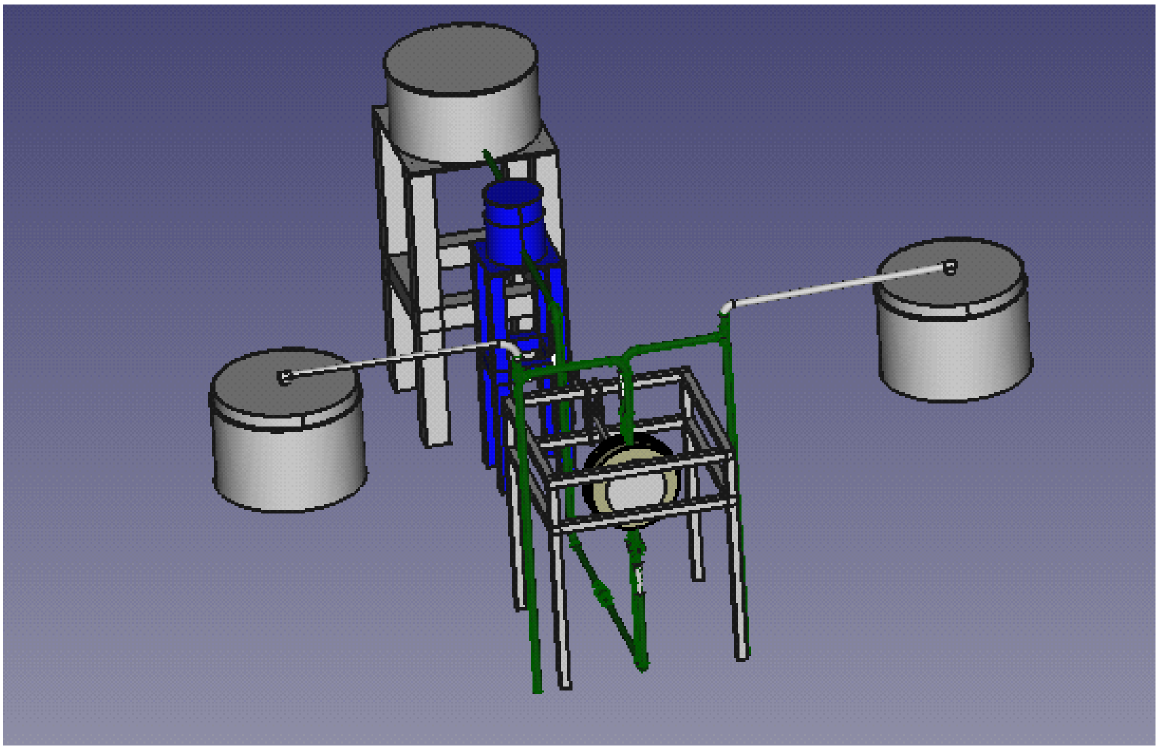
Cost of materials

منظومة تحليل الكهربائي للماء (Electrolysis Unit)

Material	Suppliers	Prices	Pictures
Nickel	نوفل	1 kg = 2.5 $	
	Alibaba	1kg = [15$ - 40$]	
Stainless	نوفل	1kg = 4.5$	
	Alibaba	1 kg = 2.3$	
Diaphragm	Alibaba	Piece = [20$ - 500$]	

7.3.4 From report 10 Nov 2018 (Samer Youcef)

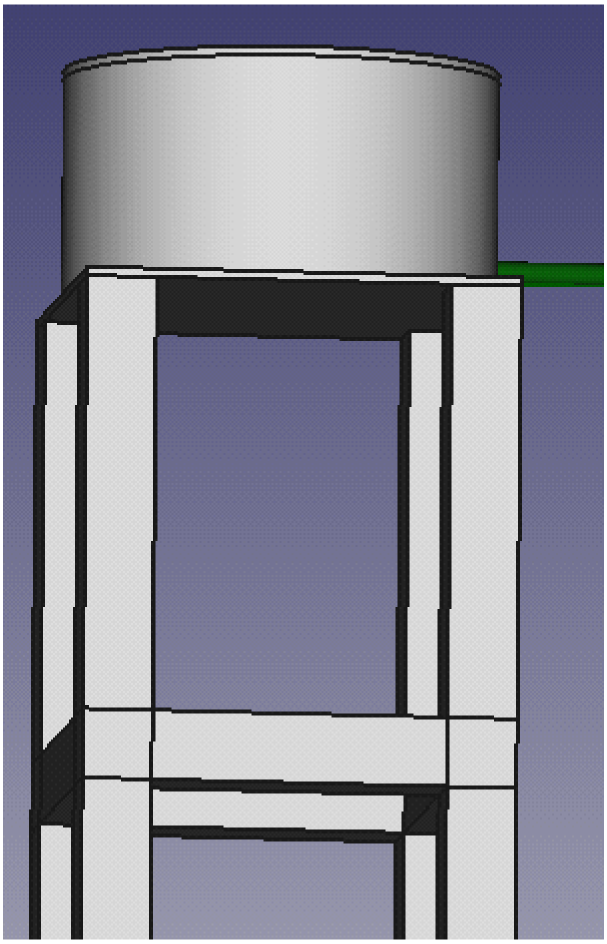
electrolyser 201018 - Copy (16).FCStd



R; THE GREEN PIPES <BBR 20> ARE BOUGHT TOGETHER USING A SPECIFIC MELTING MACHINE ,THAT COULD REACH UP TO 320 C IN ORDER TO JOIN THE PIPES TOGETHER THREW OUT THE SYSTEME , THEIR MAIN ROLE IS TO TRANSPORT WATER , AND THEY ARE FAMOUS WITH A DURABILITY THAT COULD REACH ABOUVE THE 100 YEARS LIFE SPEND MARK ; AND FOR THE WHITE PIPES THEY ARE BASICLLY PLAKSI MATERIAL,FLEXIBILE, DURABLE, AND ARE USED TO TRANSPORT GAS, AND THE SYSTEME IS MANUFACTURED IN A WAY THAT ALLOWS YOU TO SEPERATE PARTES FROM ONE ANOTHER ,WITHOUT GETTING BOUNDED BY THE PIPES ,ASSURING A GREAT DEAL OF FREEDOM.

منظومة تحليل الكهربائي للماء (Electrolysis Unit)

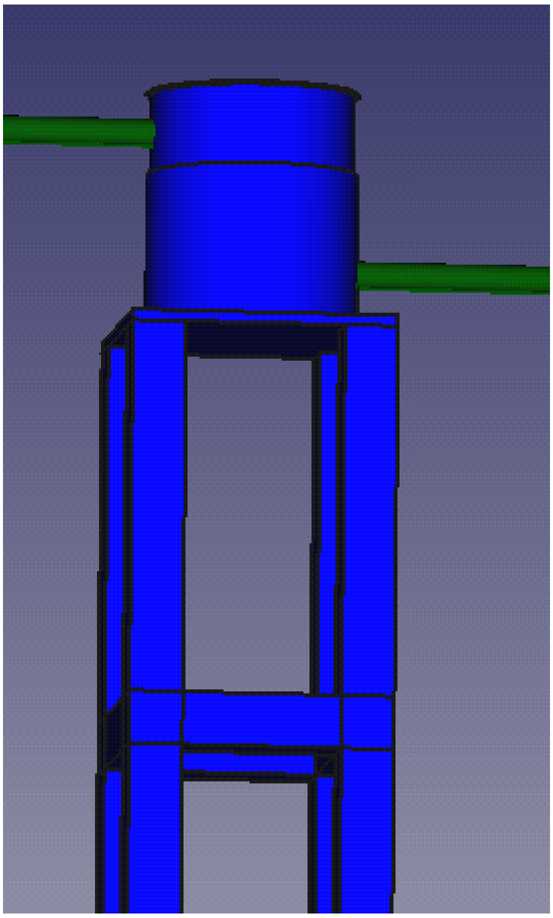
big tank.FCStd



A WATER TANK AT 50 cm OF DIAMETRE , STANDING ON A 90cm HEIGHT TABLE , WE ATTACHED A WATER TAP TO IT , CONTROLING THE WATER QUANTITY IN THE SYSTEME

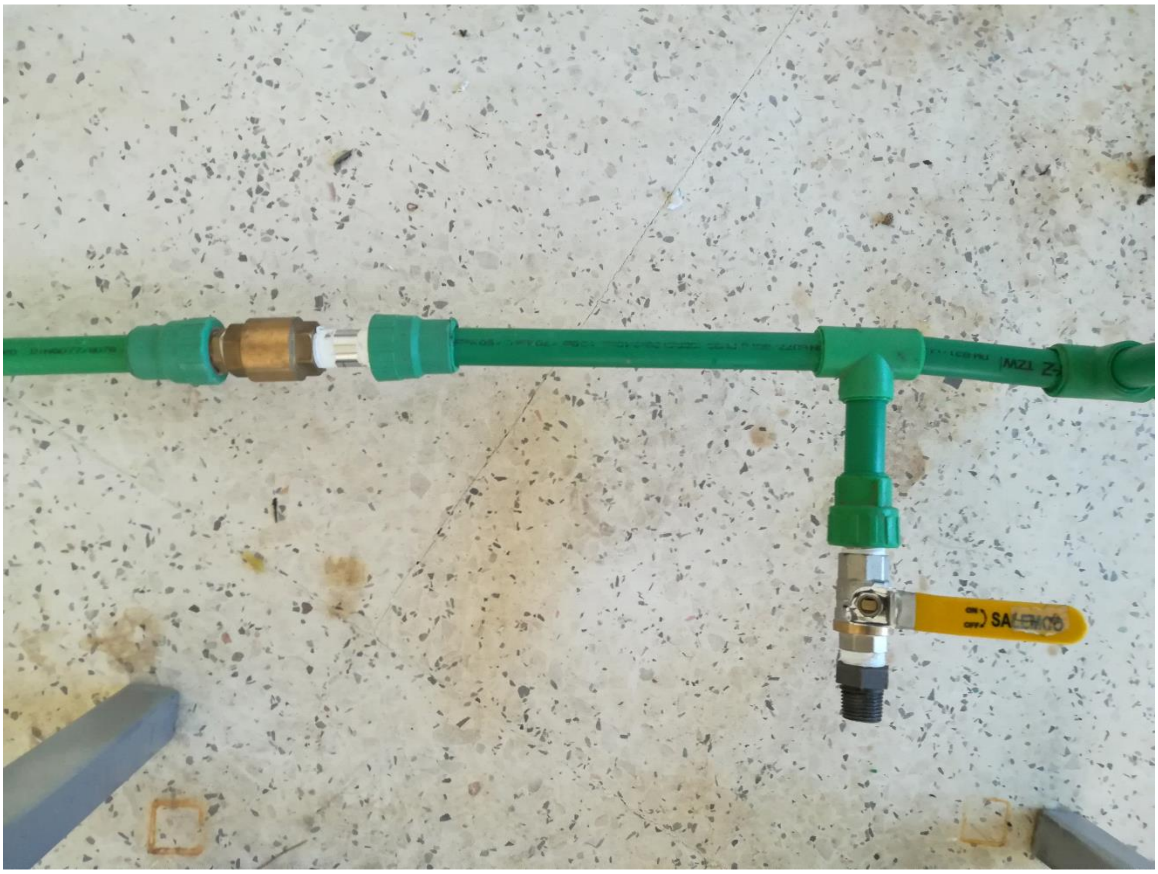
.

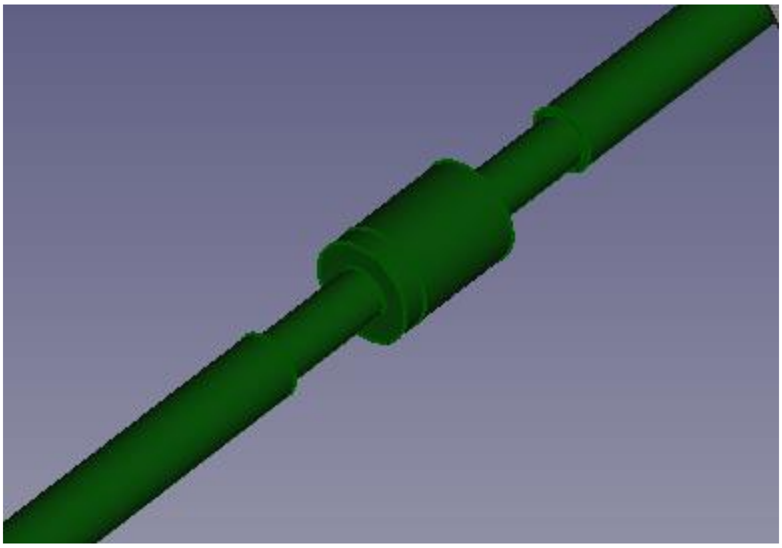
منظومة تحليل الكهربائي للماء (Electrolysis Unit)



small tank (2).FCStd

A REALTIVLY SMALLER TANK , BUT SIZE DOSEN'T ALWAYS MATTER, THIS TANK HAS NO WATER TAP , IT'S MAIN ROLE IS CONTROLING WATER LEVEL WITHIN THE SYSTEME , THREW A SPECIFIC WATER LEVELING INTRUMENT(FAWAYSHA); IT HAS LESS THEN 20cm IN DIAMETER, AND STANDING AT A TABLE HEIGHT OF 70cm .



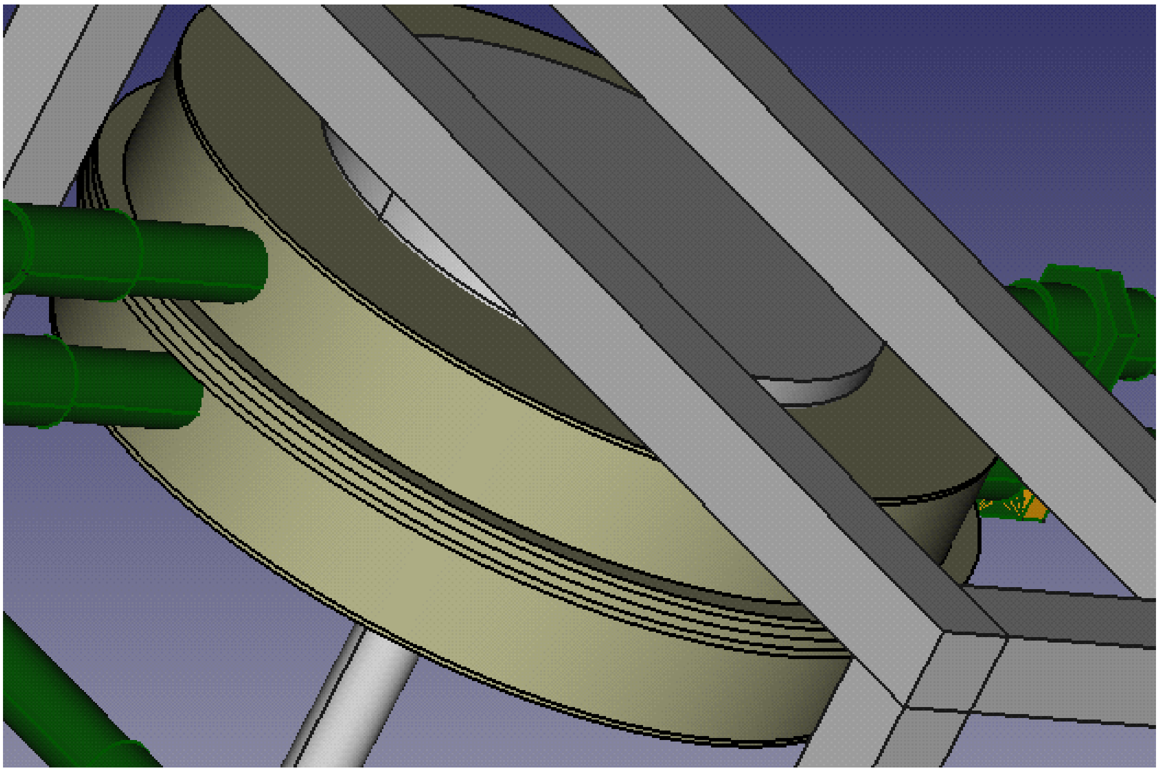


stop check valve.FCStd

A STOP CHECK VALVE, PREVENTING WATEER FROM TURNING BACK TO THE DIRECTION OF IT'S SOURCE, PLAYING A KEY ROLE IN THE STABILITY OF THE WATER IN THE SYSTEME, INCREASING LEVEL CONTROLING PRESICION; AND TO THE RIGHT WE HAVE A WATER TAP, WICH REPRESENT THE SOUL EXIST OF THE WATER FROM THE SYSTEME, WHEN WANTED

منظومة تحليل الكهربائي للماء (Electrolysis Unit)

stainless steal plates.FCStd

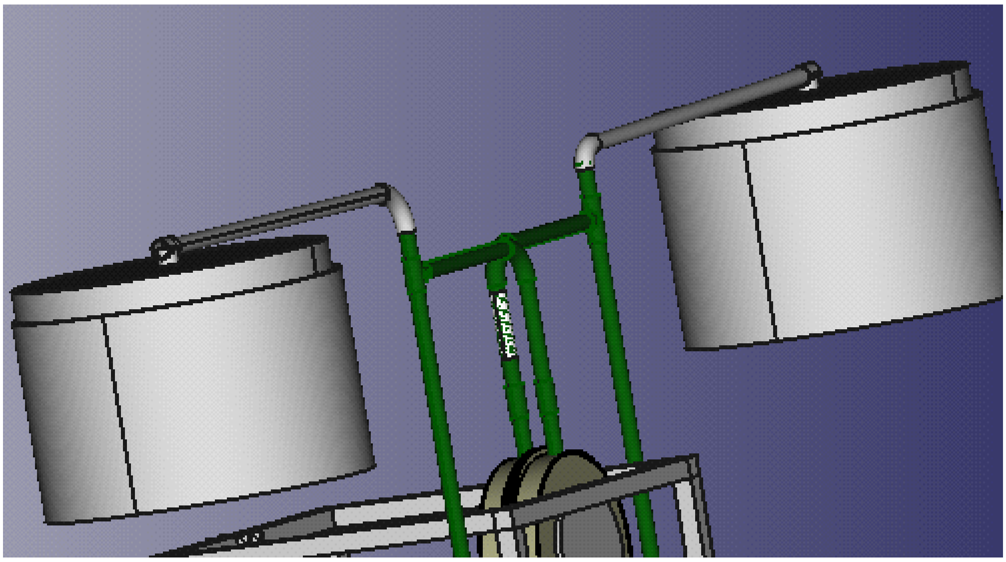


THE MAIN PART OF THE SYSTEME, 2 STAINLESS STEAL PLATES(D=30cm,edge:L,l=4mm,h=4 cm) PRESSED TOGETHER , LAYS IN BETWEEN THEM 2 RUBBER JOINTS TO ENDURE THE MASSIVE PRESSURE , AND THESE JOINTS ARE IDEAL IN PREVENTING ANY PENETRATION, BETWEEN THE PALTES .

منظومة تحليل الكهربائي للماء (Electrolysis Unit)

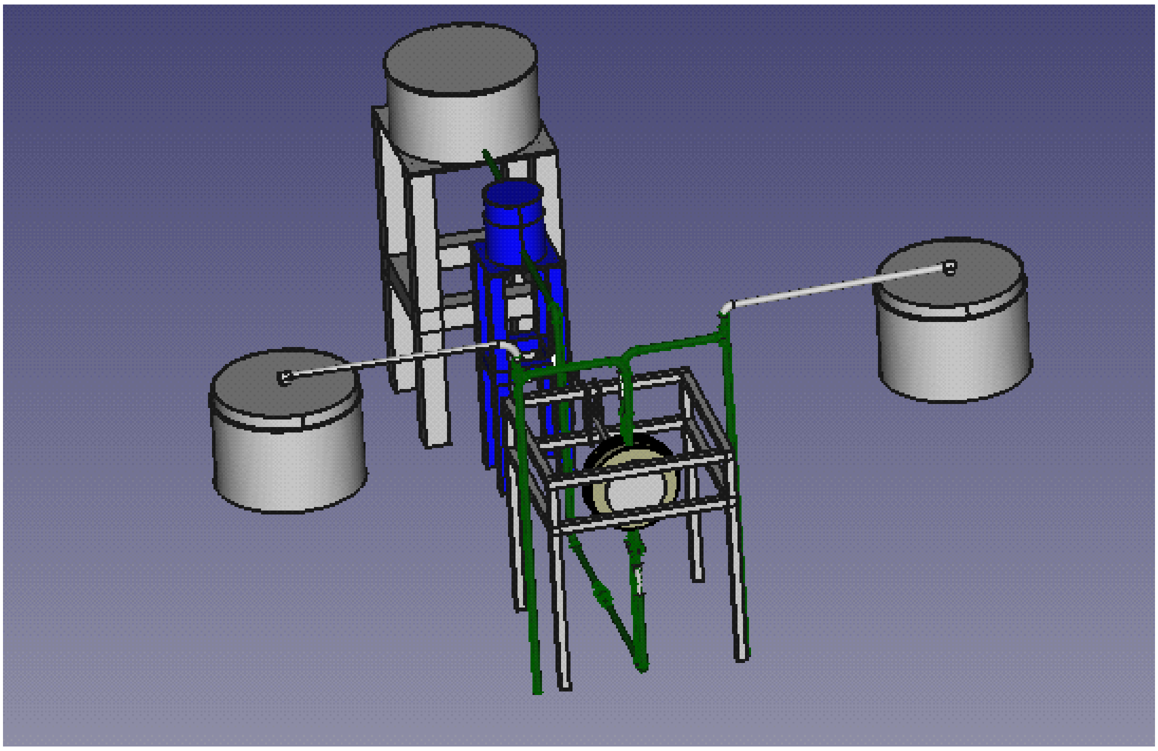
منظومة تحليل الكهربائي للماء (Electrolysis Unit)

pressure table.FCStd



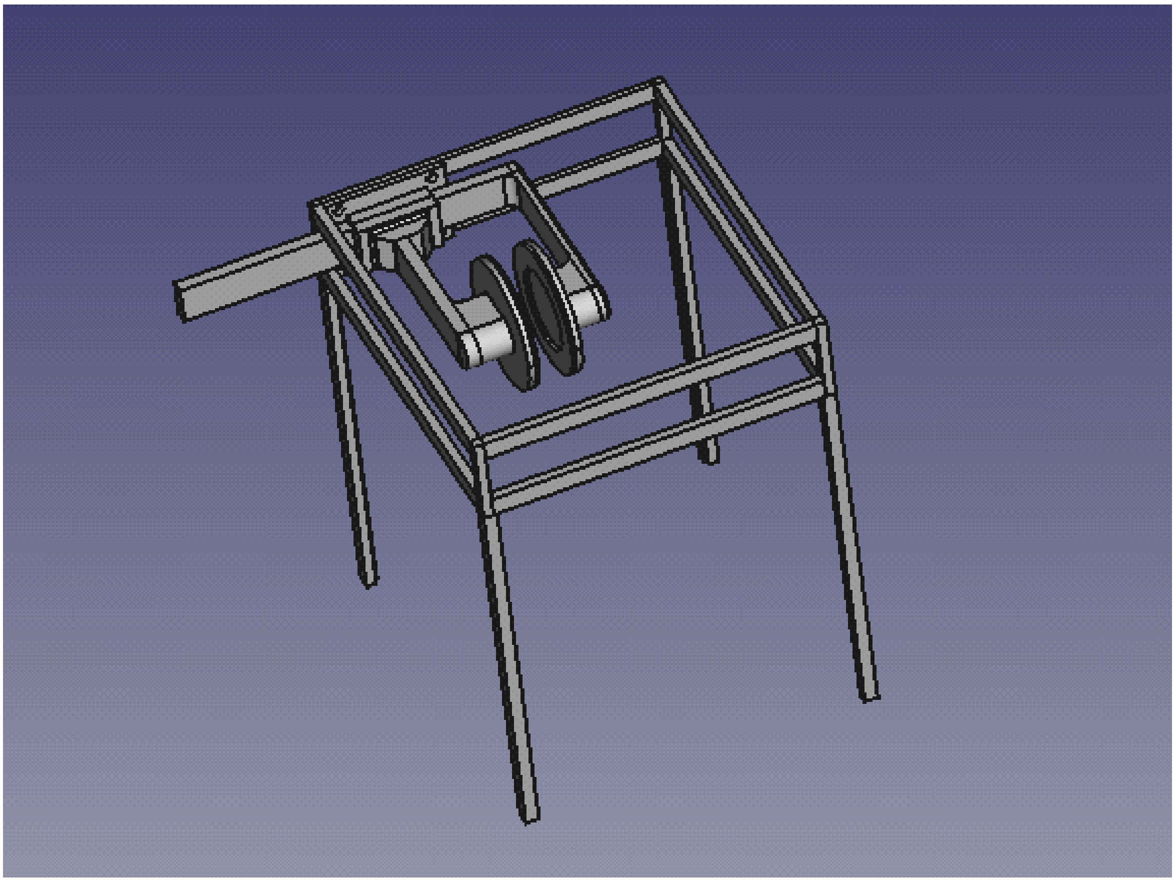
AFTER THE DECOMPOSASTION PROCESS, GAS WILL START FLOATING INSIDE THE PLAKSI PIPES , WICH WILL EVENTUALLY BE STOCKED IN THE PRESSURE CHAMPER BY A SPECIFIC WATER METHODE, EACH ONE OF THIS 2 CHAMPERS CONTAINS DIFERENT GASES (H2,O2).

منظومة تحليل الكهربائي للماء (Electrolysis Unit)



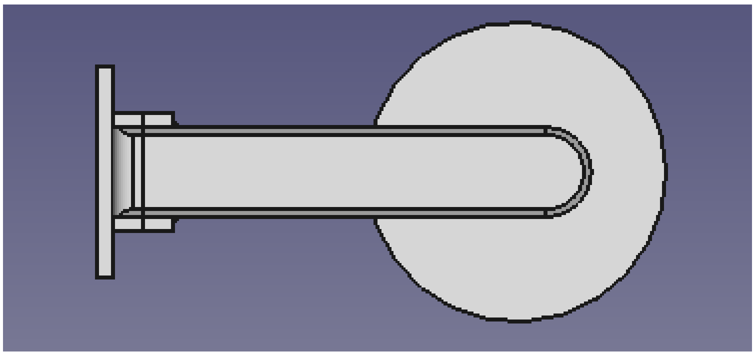
R; THE GREEN PIPES <BBR 20> ARE BOUGHT TOGETHER USING A SPECIFIC MELTING MACHINE ,THAT COULD REACH UP TO 320 C IN ORDER TO JOIN THE PIPES TOGETHER THREW OUT THE

Electrolyser base :180918



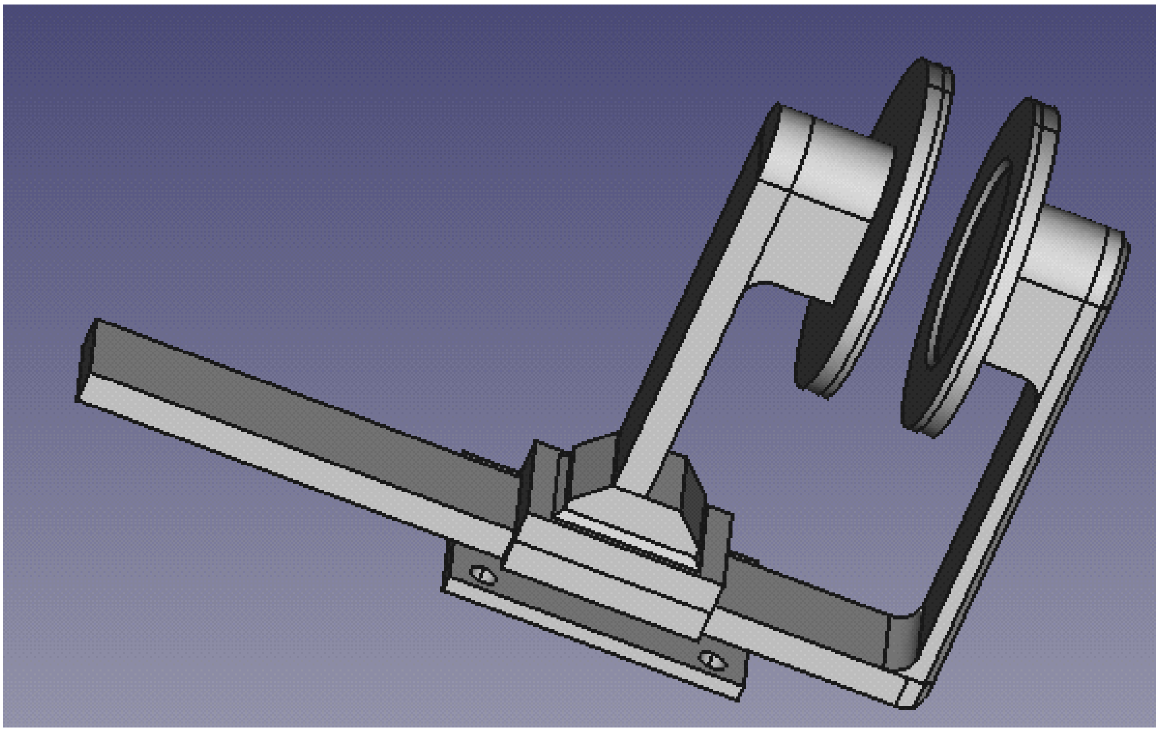
ارتفاع الاقدام :60 سنتمتر

الطول والعرض :55 سنتمتر



قطر الدائرة :20 سنتمتر

السماكة: 10 ملمتر

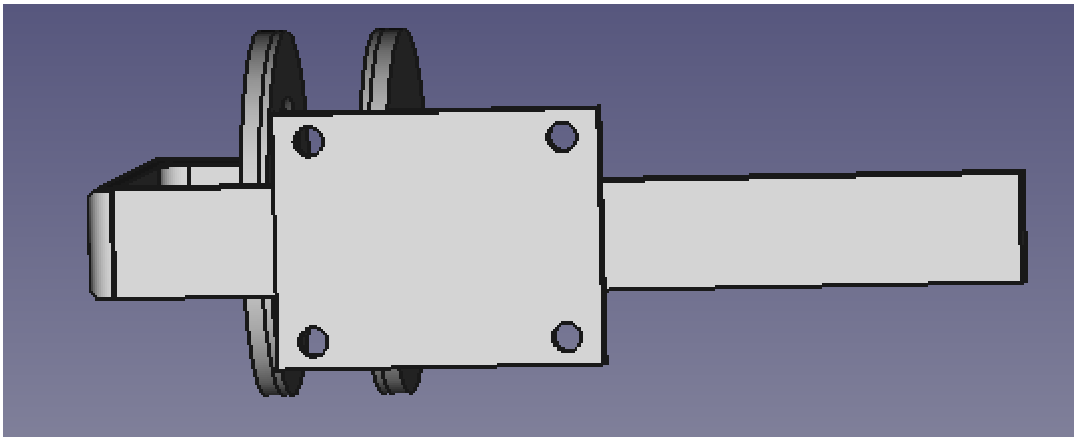


قطر الدائرة الداخلية : 12 سنتمتر

السماكة :5 ملمتر

ارتفاع الدائرة : 25 سنتمتر

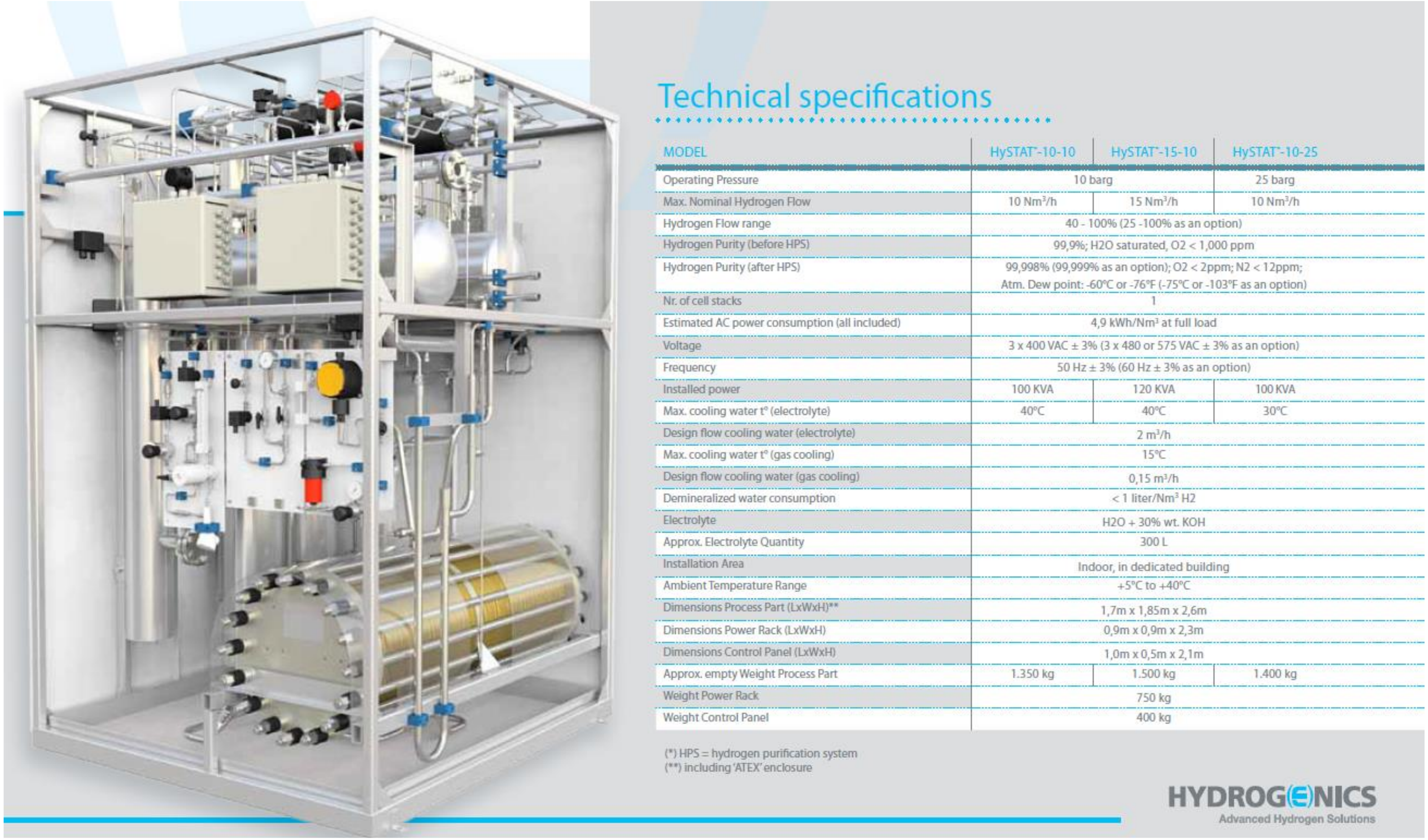
تبعد الدائرة الاولى عن الثانية كحد اقصى : 50 سنتمتر



طول : 14 سنتمتر

عرض :18 سنتمتر

7.4 Hydrogenics electrolyzer



Technical specifications

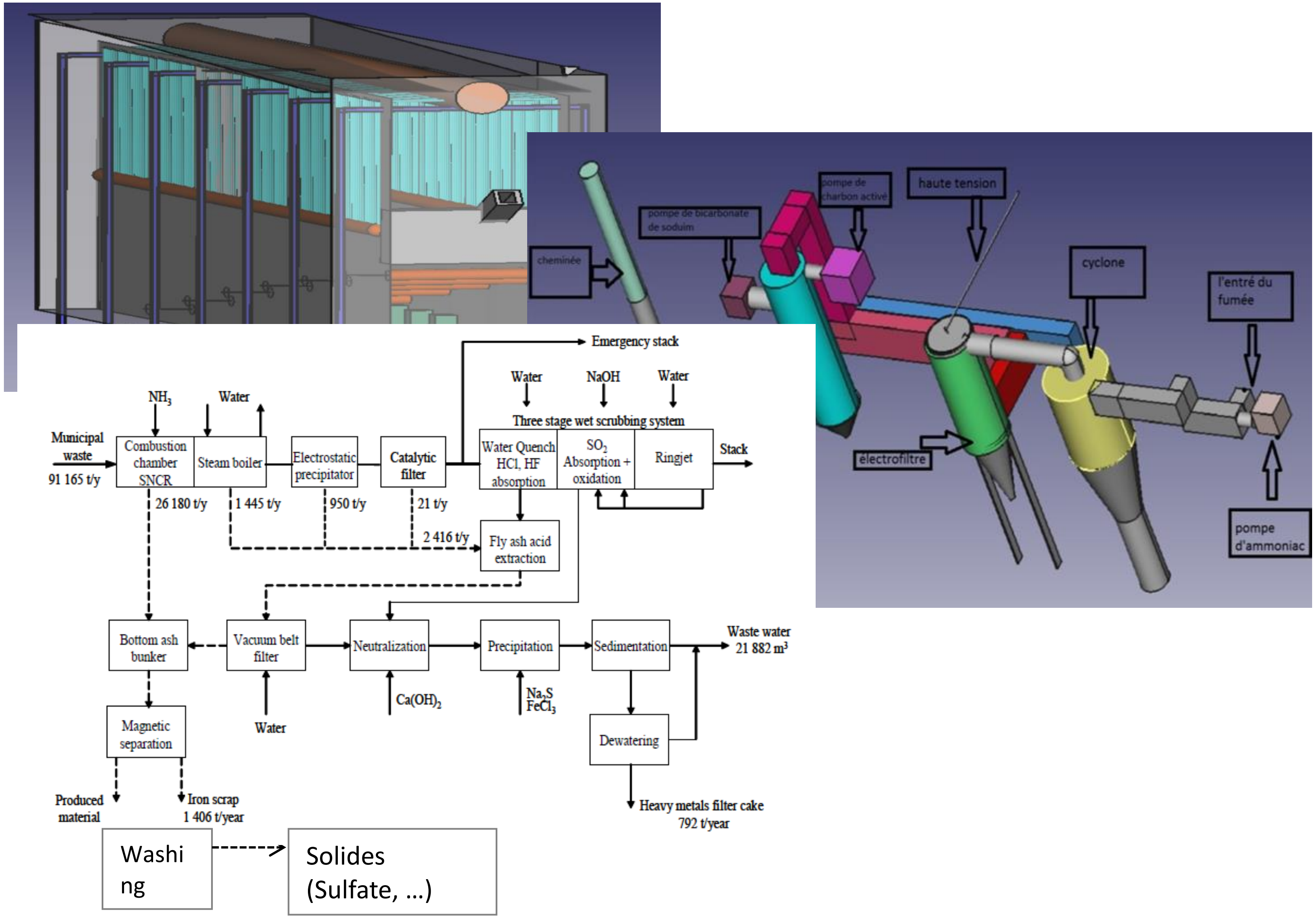
MODEL	HySTAT™-10-10	HySTAT™-15-10	HySTAT™-10-25
Operating Pressure	10 barg		25 barg
Max. Nominal Hydrogen Flow	10 Nm³/h	15 Nm³/h	10 Nm³/h
Hydrogen Flow range	40 - 100% (25 -100% as an option)		
Hydrogen Purity (before HPS)	99,9%; H2O saturated, O2 < 1,000 ppm		
Hydrogen Purity (after HPS)	99,998% (99,999% as an option); O2 < 2ppm; N2 < 12ppm; Atm. Dew point: -60°C or -76°F (-75°C or -103°F as an option)		
Nr. of cell stacks	1		
Estimated AC power consumption (all included)	4,9 kWh/Nm³ at full load		
Voltage	3 x 400 VAC ± 3% (3 x 480 or 575 VAC ± 3% as an option)		
Frequency	50 Hz ± 3% (60 Hz ± 3% as an option)		
Installed power	100 KVA	120 KVA	100 KVA
Max. cooling water t° (electrolyte)	40°C	40°C	30°C
Design flow cooling water (electrolyte)	2 m³/h		
Max. cooling water t° (gas cooling)	15°C		
Design flow cooling water (gas cooling)	0,15 m³/h		
Demineralized water consumption	< 1 liter/Nm³ H2		
Electrolyte	H2O + 30% wt. KOH		
Approx. Electrolyte Quantity	300 L		
Installation Area	Indoor, in dedicated building		
Ambient Temperature Range	+5°C to +40°C		
Dimensions Process Part (LxWxH)**	1,7m x 1,85m x 2,6m		
Dimensions Power Rack (LxWxH)	0,9m x 0,9m x 2,3m		
Dimensions Control Panel (LxWxH)	1,0m x 0,5m x 2,1m		
Approx. empty Weight Process Part	1.350 kg	1.500 kg	1.400 kg
Weight Power Rack	750 kg		
Weight Control Panel	400 kg		

(*) HPS = hydrogen purification system
(**) including 'ATEX' enclosure

HYDROGENICS
Advanced Hydrogen Solutions

8 Ashes Recycling Unit

8.1 First Conception Dec 2017



8.2 Heavy Metals extraction unit[17]

8.2.1 COPPER EXTRACTION[18]

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[17] Maysaa Kamareddine, Concept for Ashes Recycling Unit, May 2018

[18] Murdoch Mackenzie, Henkel Australia Pty ltd , THE SOLVENT EXTRACTION OF SOME MAJOR METALS - AN OVERVIEW (thesolve.pdf) (about 1998)

REFERENCES

(1) R.B. Sudderth and G.A. Kordosky, "Some Practical Considerations in the Evalaution and Selection of Solvent Extraction Reagents" Chemical Reagents in the Mineral Processing Industry. Ed. Malhotra and Riggs. SME 1987

(2) J.M.W. Mackenzie, "Uranium Solvent Extraction Using Tertiary Amines" ALTA 1997 Uranium Ore to Yellow Cake Seminar. ALTA Metallurgical Services, Melbourne Australia.

(3) K. Soldenhoff, N. Hayward and D. Wilkins, "Direct Solvent Extraction of Cobalt and Nickel from Laterite Acid-Pressure Leach Liquors" EPD Congress 1998. Ed. B.Mishra (The Minerals, Metals and Materials Society, AIME) 1998 p153-165

(4) G.M. Ritcey, "Commercial Processes for Nickel and Cobalt" In Handbook of Solvent Extraction. Ed Lo, Baird, and Hansen. John Wiley and Sons 1983. P 673

(5) J.M.W. Mackenzie and M.J.Virnig, "Recovery of Nickel from Ammoniacal Solutions Using LIX® 84-I" Proceedings of ALTA Nickel /Cobalt Pressure Leaching and Hydrometallurgy Forum, May 1996. Perth West Australia. ALTA Metallurgical Services Melbourne.

(6) J.M.W. Mackenzie and M.J.Virnig, "Extraction of Nickel from Ammoniacal Leach Solutions: Extractant and Solution Chemistry Issues" Proceedings of ALTA 1998 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum. May 1998. Perth West Australia. ALTA Metallurgical Services Melbourne

(7) M.J.Price and J.G.Reid, "Separation and Recovery of Nickel and Cobalt in Ammoniacal Systems: Process Development" Proceedings ISEC 93 , SCI London 1993 p159.

(8) M.J.Virnig, J.M.W.Mackenzie, and C.Adamson. " The Use of Guanidine – Based Reagents for the Recovery of Gold" Hidden Wealth. South African Institute of Mining and Metallurgy. 1996 p151

(9) R.L.Movsowitz, R.Kleinberger, and E.M.Buchalter, "Application of Pulsed Colums for Uranium SX From Pilot to Industrial Columns" ALTA 1997 Uranium Ore to Yellowcake Seminar. ALTA Metallurgical Services, Melbourne 1997

(10) T.A.Post, M.A.Giralico, M.C.Greaves, and G.M.Frazer, "Operational Results from Optimised Lightnin SX Pumper and Auxilliary Mixer Designs" ALTA 1996 Copper Hydrometallurgy Forum. Brisbane 1996. ALTA Metallurgical Services Melbourne.

(11) B.Nyman, R.Kuusisto, P.Taipale and J. Lyyra, "Emphaisi on Feed End Settling in Outokumpu's VSF Mixer-Settler" Ibid.

Copper extractants for acid leach solutions are exclusively oximes. For extraction from ammoniacal solutions beta diketones may be used. The chemistry of oxime extraction of copper is relatively simple:

$$2RH_{(org)} + Cu^{+2} + SO_4^{-2} \rightleftharpoons R2Cu_{(org)} + 2H^{+} + SO_4^{-2}|$$

Note the following points about this equation:

When M(2+) is extracted two hydrogen atoms are released.

Extraction of 1.0 gpl Cu produces 1.5 gpl H_2SO_4. There are other reactions which take place in copper extraction which can influence extraction and stripping.

8.2.1.1 • Buffering of the aqueous

Dissociation of H_2SO_4:

$$H_2SO_4 \rightleftharpoons H^{+} + HSO_4^{-}$$

$$HSO_4^{-} \rightleftharpoons H^{+} + SO_4^{-2}$$

This dissociation depends on the SO4.

8.2.1.2 Concentration and salts such as aluminium

Sulphate or magnesium sulphate can drive this reaction to the left and reduce the H+ concentration which enhances copper extraction. For this reason highly buffered solutions will yield better copper extraction than non buffered solutions.

8.2.1.3 Dimerisation of the oxime

Oximes can form dimers in the organic phase and this can influence the extraction.

8.2.1.4 Equilibrium Modifiers

These are used in all commercial extractants based on aldoximes and play a most significant role in the extraction of copper influencing not only the equilibrium but also the physical properties of the organic.

8.2.1.5 Extractant Types

Oxime based extractants for copper are largely based on salicyaldoximes which have been modified with one of three modifier types. Examples of the three main extractant types currently in use are:

1. LIX® 984N

A mixture of 2-hydroxy-5-nonylacetophenone oxime and 5-nonylsalicylaldoxime in a

high flash diluent. The acetophenone oxime modifies the aldoxime and also performs as an extractant in its own right.

2. Acorga® M5640

5-Nonylsalicylaldoxime modified with an ester, 2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate (TXIB) in a high flash diluent.

3. LIX® 622N

5-Nonylsalicylaldoxime modified with tridecyl alcohol in a high flash diluent. Each of the extractants marketed by the major chemical suppliers has been designed for a specific type of PLS with regard to pH and copper tenor. Used under the conditions for which they were designed they all deliver very similar copper net transfer values. The physical properties of the various types of extractant do show some differences with the aldoxime/ketoxime mixtures such as LIX984N showing lower entrainments and greater tolerance to crud than the other reagents when treating some types of PLS. The vol% concentration of the commercially available extractants is limited by organic viscosity constraints to about 30-33% and this means that the maximum net transfer of copper will be about 10g/l. For leach solutions containing significantly higher copper tenors than this the throughput O/A ratio will have to be increased above 1.0. Typical copper and acid concentrations for an SX plant treating a dump leach solution of 3.0g/l and pH1.8 are shown in Figure 4.

8.2.1.6 Copper solvent extraction plant configurations

A variety of circuit configurations are used.

- **2E X 1S**

The usual circuit for heap leach plants

- **2E X 2S**

Used where the copper tenor is above about 7-10 g/l or the PLS pH is less than about 1.2. The decision to use a second strip stage is influenced by the life of the project and the sensitivity of the circuit to the copper tenor of the raffinate. Agitation leach plants for example are sensitive to the loss of copper in a raffinate bleed or in the wash liquor used in the solid liquid separation stages.

- **3E X 2S**

These can be justified when the PLS has a very high copper tenor, say above 20- 25g/l and a high 93% plus copper recovery is desired. It is possible to use a 2EX2S circuit under these conditions but the throughput O/A ratios will be high, in excess of 2.5:1 and the capital cost of the 2EX2S plant may be higher than that of the 3EX2S plant. The 3EX2S plant will also be much more flexible in operation.

- **2E X 1W X 1S**

The wash stage is used to remove entrained impurities, usually chloride, and entrained and chemically loaded iron.

- **2E X 1P X 1S**

Series parallel circuits are used to treat high volumes of low tenor leach solutions. The parallel stage is often retrofitted to maintain copper production when the copper tenor of the PLS falls below project design and there is also the possibility to increase the volume of the PLS flow.

Extractant concentrations are higher and copper recoveries are lower in series parallel circuits than in series circuits. Examples of these circuit configurations are shown in Figure 5.

8.2.1.7 Computer modeling of copper extraction circuits

Copper SX circuits have been modeled using a number of techniques. One such model is Henkel's IsocalcTM TM programme which applies the stability constants for the equilibrium reactions involved in copper extraction to calculate the extraction isotherm for a given leach solution and circuit organic and then applies the McCabe Thiele construction to predict circuit operation. A typical Isocalc print out is shown in Figure 6.

Isocalc can be used in many ways by both project design and plant operating personnel.

- Copper recovery may be predicted for a given PLS, circuit configuration and vol% extractant concentration.

- The reagent inventory cost and copper recovery may be predicted for a variety of circuit configurations.

- A wide range of "what if?" situations may be examined, eg. what if the PLS pH changes from 1.8 to 1.5?

- Operating circuit profiles may be compared with Isocalc predictions. This comparison may indicate the presence of errors in the assumed or measured parameters of the plant, eg. the vol % extractant analysis may be in error.

8.2.1.8 Extractant stability

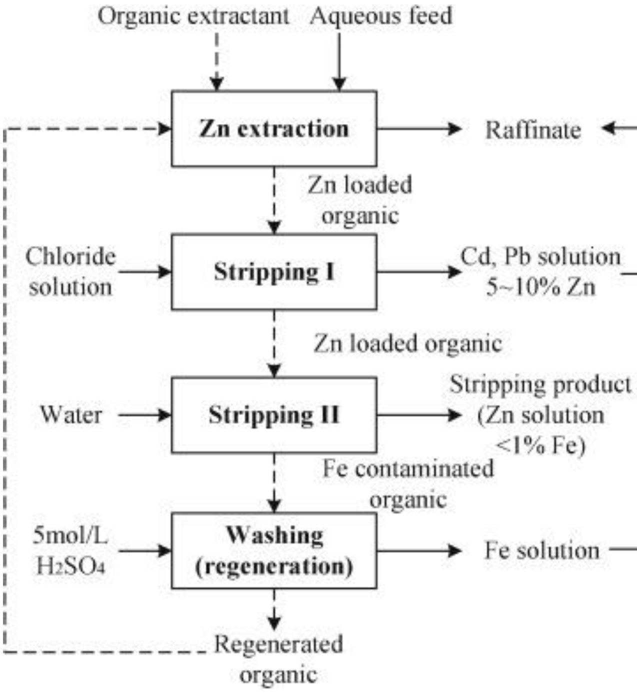
The oxime based extractants used to recover copper exhibit high chemical stability under normal operating conditions. Chemical attack can take place in the high acid concentrations in strip. Under normal operating temperatures this is not excessive however the degradation rate doubles for every 10oC increase in temperature. At 30oC the half-life of most copper extractants exceeds 150 days and it is only above 50oC that chemical degradation may become an issue. Manganese contamination of the tankhouse may, if the iron level of the tankhouse electrolyte is low, result in permanganate formation and this species can severely degrade both the extractant and the diluent. Bacterial oxidation of the diluent to form carboxylates is relatively common and these ay have a negative effect on the physical and iron transfer characteristics of the organic.

8.2.2 Nickel extractants

Unlike U/copper extraction where one type of extractant and circuit predominates there is a number of potential nickel extractants and circuit configurations. Sulphide nickel is usually treated using pyrometallurgical routes but in recent years there has been intensive activity in the development of hydrometallurgical routes for both sulphide concentrates and laterites. Nickel deposits can contain valuable quantities of cobalt and copper and these must also be recovered by SX if they are present in sufficient quantity.

Direct solvent extraction of copper, cobalt and nickel from acid leach solutions using oximes, phosphinic acids and versatic acids to extract copper, cobalt and nickel in sequence. While this circuit may function on leach solutions derived from sulphide concentrates, laterite leach solutions contain significant manganese and magnesium, both of which are extracted by phosphinic acid extractants. In addition the aqueous solubility of versatic acid at the pH used for extraction necessitates the inclusion of a versatic acid recovery stage.

8.2.3 ZINC, CADMIUM, LEAD EXTRACTION



8.2.4 SOLVENT EXTRACTION- SOME OPERATIONAL AND EQUIPMENT ISSUES

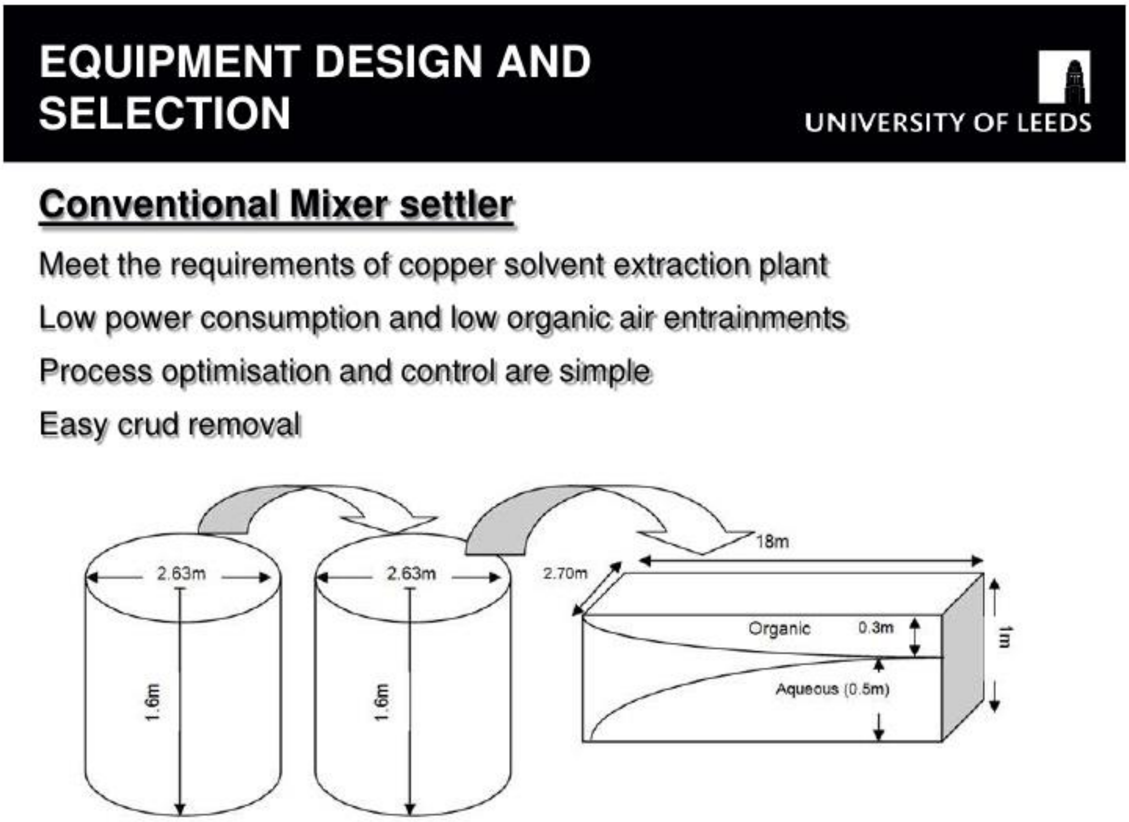
8.2.4.1 Contactor Design

For the major metals recovered by solvent extraction the mixer-settler contactor design predominates. However there is a range of mixer settler designs available and in recent years there has been some attention refocused on the use of pulsed columns for plants using the kinetically fast ion- exchange extractants. For the chelating extractants which require a minimum of two minutes' mixer residence time in a well-stirred incinerator, columns have not yet become commercially acceptable. Kvaerner have marketed a variety of the mixer – settler called the combined mixer- settler. As with columns, this unit has only found acceptance for ion-pair extractant systems. Some features of mixer-settlers and columns are given below.

Mixer Settlers

- Well established with literally hundreds of operating units.
- Design parameters are well established and very large units treating over 1000 cubic metres per hour of PLS can be designed from bench scale tests.
- Excellent mixing characteristics with control of the optimum droplet size claimed to be possible with modern turbine designs.
- Prediction of capital and operating costs is accurate.

- The phases are readily accessible for sampling and examination in situ.
- Several design varieties are available such as the Bateman Reverse Flow Settler, the Krebs unit and the Outokumpu VSF mixer settler. The Bateman and Krebs units offer the advantage of installing all of the mixers in a row avoiding the extra piping, walkways and civils involved in the typical head to toe mixer arrangement for conventional mixer settlers. The Outokumpu unit uses a special design of mixer, the vertical smooth flow spiral mixer and pumps the phases from adjacent stages using a dispersion overflow pump. Low power requirements and low entrainments are claimed for the Outokumpu unit.



EQUIPMENT DESIGN AND SELECTION

UNIVERSITY OF LEEDS

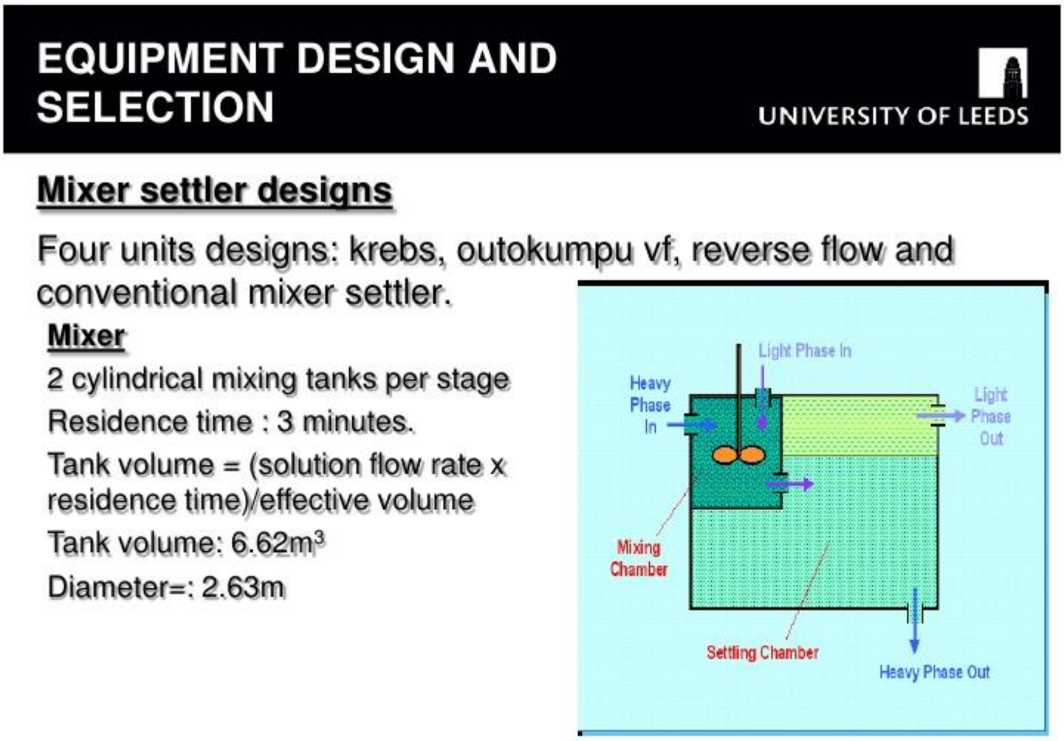
Conventional Mixer settler

Meet the requirements of copper solvent extraction plant

Low power consumption and low organic air entrainments

Process optimisation and control are simple

Easy crud removal



EQUIPMENT DESIGN AND SELECTION

UNIVERSITY OF LEEDS

Mixer settler designs

Four units designs: krebs, outokumpu vf, reverse flow and conventional mixer settler.

Mixer

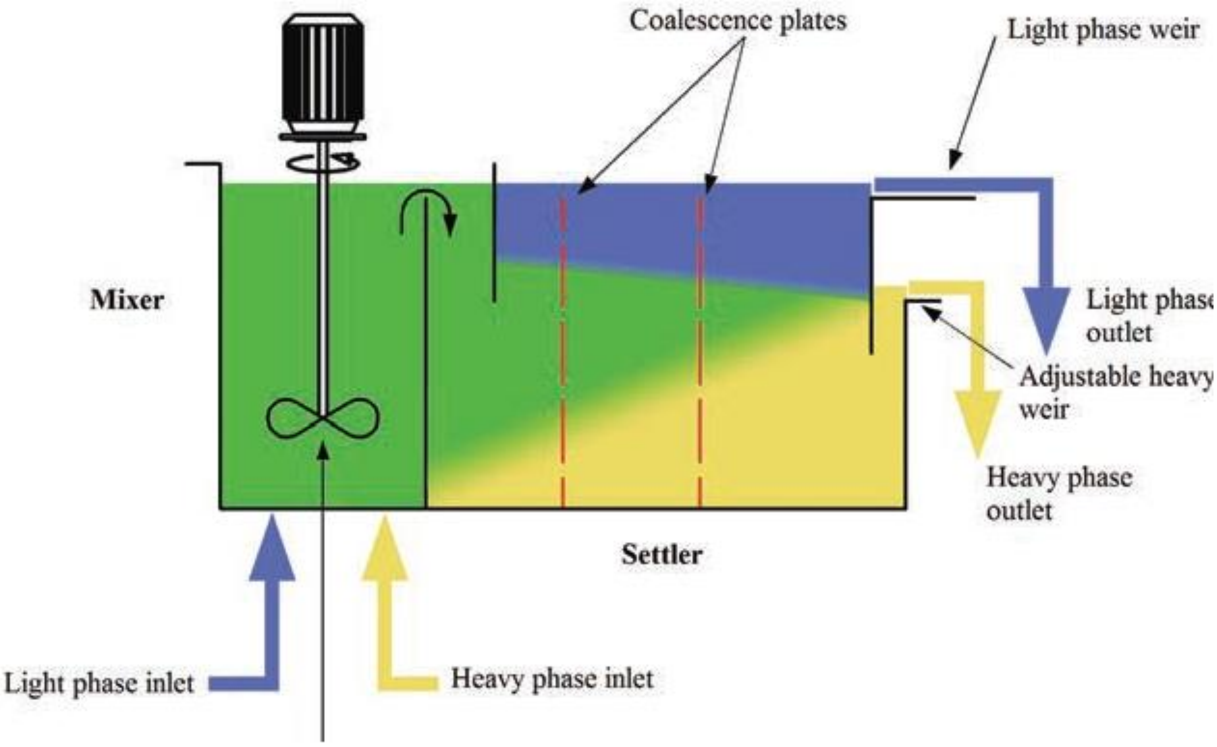
2 cylindrical mixing tanks per stage

Residence time : 3 minutes.

Tank volume = (solution flow rate x residence time)/effective volume

Tank volume: 6.62m^3

Diameter=: 2.63m



Column Contactors

Advantages claimed for the column contactor include:

- Low area requirements
- Multiple stages within one unit
- Few moving parts
- Low entrainment
- Good vapor conservation

Column installations require piloting for each installation and the flooding conditions for the column must be determined. Recently Olympic Dam Corporation in South Australia has installed a large column plant for uranium extraction. The long residence times in a column compared to a mixer settler can influence the selectivity of the extraction if contaminants have slow extraction kinetics. The main features of conventional mixer – settlers and pulsed columns are shown in Figures 12 and 13.

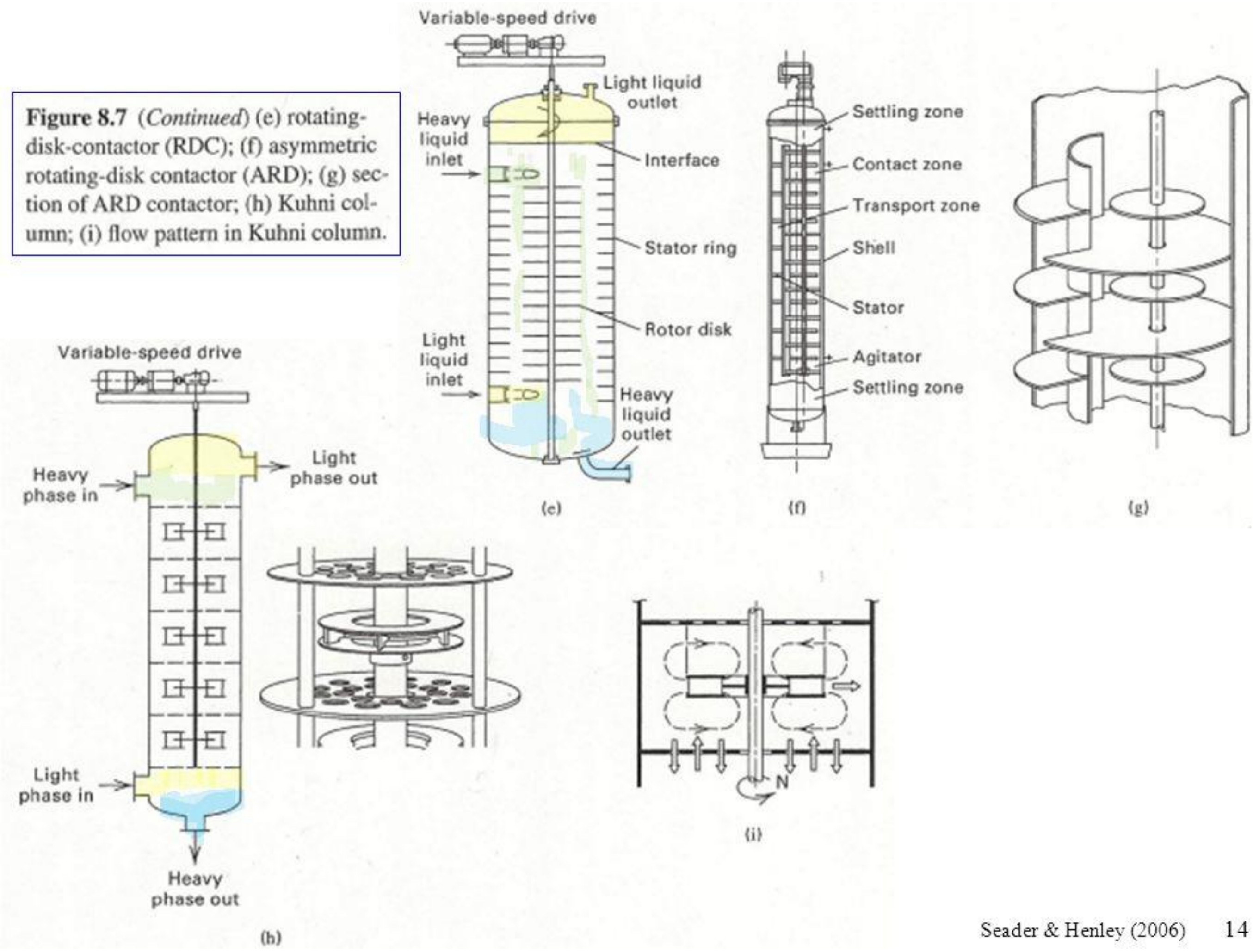
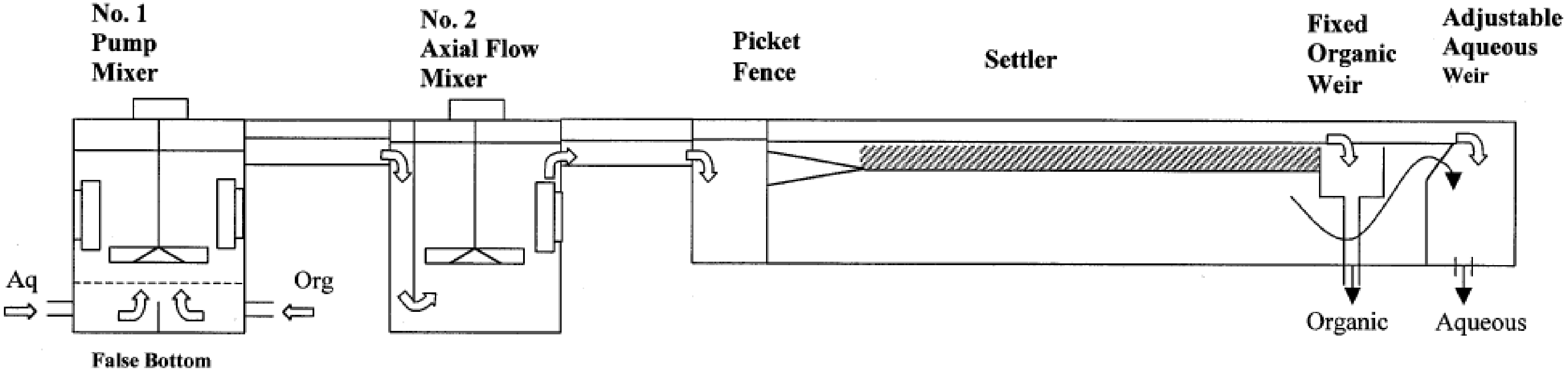


Figure 8.7 (*Continued*) (e) rotating-disk-contactor (RDC); (f) asymmetric rotating-disk contactor (ARD); (g) section of ARD contactor; (h) Kuhni column; (i) flow pattern in Kuhni column.

Seader & Henley (2006) 14

Figure 8 : OVERVIEW OF KIND OF COLUMNS

CONVENTIONAL MIXER SETTLER



MIXER DESIGN CRITERIA

Mixer O/A (use recycles if needed)	1.1
Mixer Residence Time	
Copper	2 mins 3 mins if cold
Tip Speed	250 – 300 metre/min

N^3D^2 < 20
N = rps
D = diameter in feet

SETTLER DESIGN CRITERIA

SPECIFIC FLOW RATE	4.0 – 5.0 $m^3/m^2/hr$ (Total flow)
If cold	3.0 – 3.5 $m^3/m^2/hr$
ORGANIC SPACE VELOCITY	3 – 6 cm/sec.
ORGANIC DEPTH	200 – 250 mm

From total organic flow calculate settler width from organic space velocity and organic depth.

From specific flow rate calculate settler area and settler length.

Figure 12

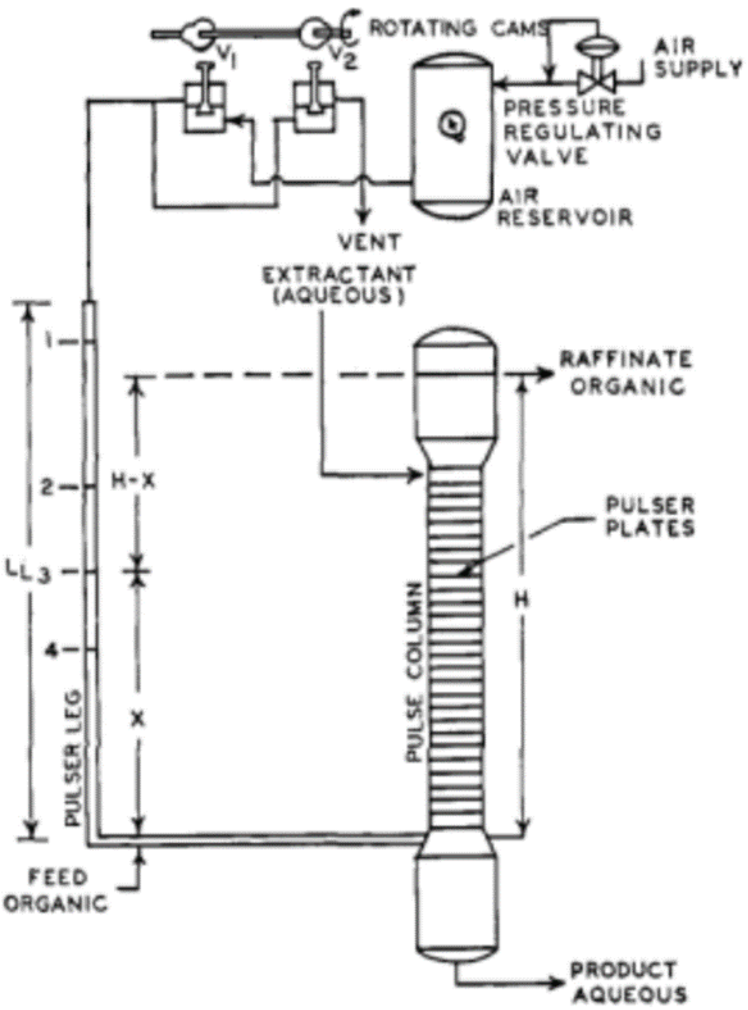
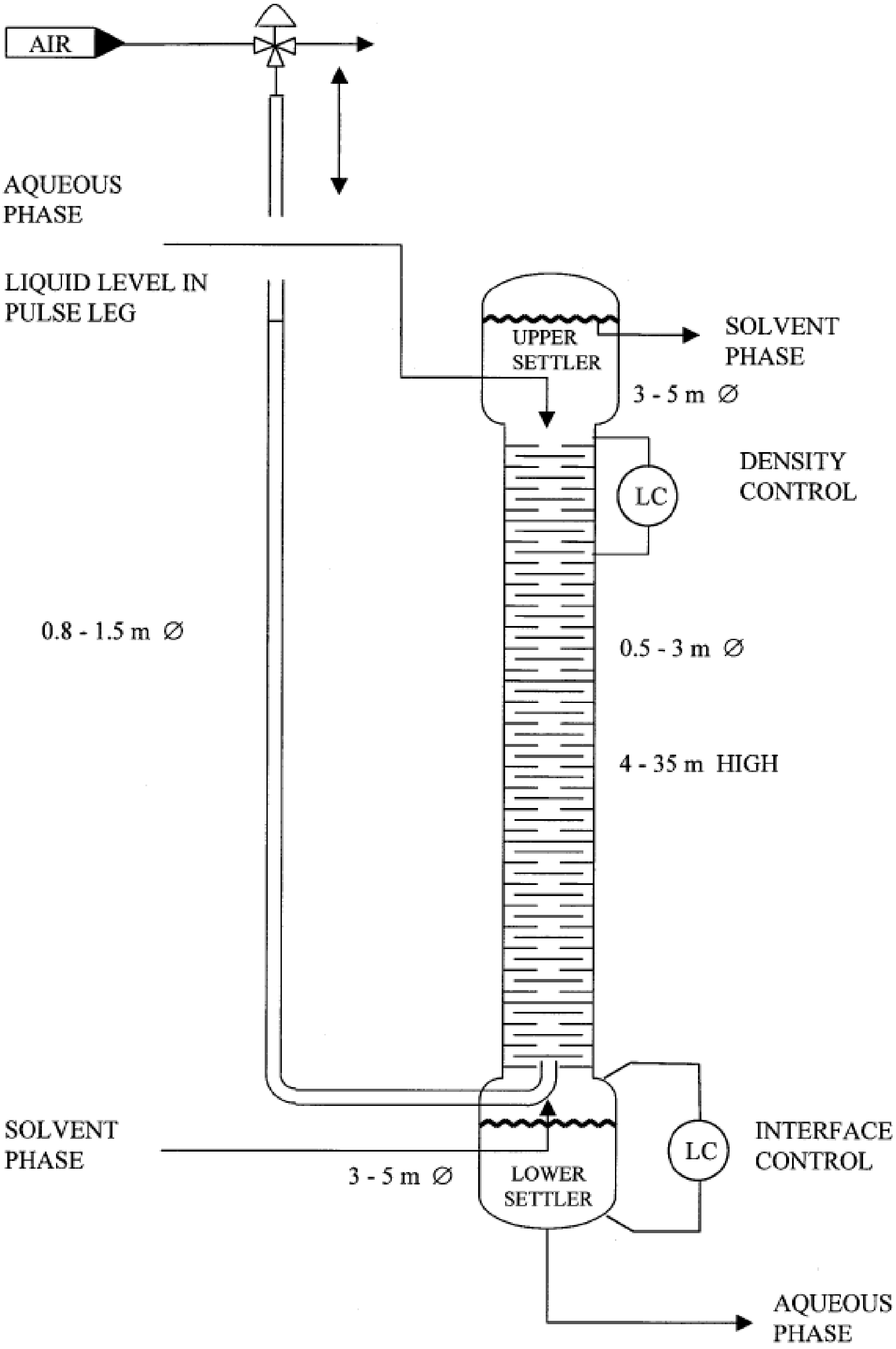


Figure 9 :pulsed column

if the fluid in the column and pulse leg are permitted to reach hydraulic equilibrium (valve 2 open), the fluid level will have reached position 1 in the leg with the fluid level maintained at the overflow point in the column. air pressure is now set and the cam started rotating. When v1 is open, v2 is closed which alternately admits and released air into and from the pulse leg. After equilibrium is reached in the system, the fluid in the leg will reach an average position 3 and will oscillate between points 2 and 4. air pressure forces the fluid down from 2 to 4 while the hydraulic head differences between the column overflow and fluid in the leg force the fluid in the leg back from 4 to 2.This interchange of fluid between the pulse leg and column provides the pulse action required in the column .Operating ranges usually encountered in amplitude area from 0.4 to 1.25 inches in the plate section of the column at frequencies from 40 to 100 cycles in minute . the poppet valve and motor are arranged with flange disconnects and electrical plugs-in for ease in replacement of unit needing maintenance. This pulsers are fitted with rotary and liquid sensing devices which close a safety in the event either sensor signals.



BATEMAN PULSED COLUMN

Figure 13

Diagram supplied with permission from Alta Metallurgical Services Pty Ltd and Bateman

Comparison between Bateman column and mixer settler[19]

Bateman column: Flux rates of 30 to 50 m3/m2*h, resulting in very small footprint requirements;

- no evaporation losses or air ingress as the units are sealed;
- improved safety of operation and lower fire risk;
- replacement of several mixer settlers by a single column for the equivalent performance;
- operation in either aqueous- or organic-phase continuity (including the possibility of dispersing the major phase in the minor phase);
- inclusion of washing or scrubbing operations in the extraction or stripping columns;
- improved phase separation in the settlers, lower entrainment losses, and reduced crud formation since mixing and mass transfer occur in a very low-shear environment;
- high tolerance of solids or crud in suspension;
- lower maintenance downtime due to few moving parts;
- reduced reagent losses, maintenance costs, and operating costs.

Since columns are particularly appropriate for systems that have rapid kinetics and do not require interstage pH control, the extraction of zinc by di(2-ethyl-hexyl) phosphoric acid (D2EHPA) is ideally suited to this application. The objectives of this study were (i) to determine whether data comparable to the previously optimised results for this system obtained using mixer settlers could be achieved for similar process conditions using a column configuration, and (ii) to validate the claimed advantages of BPCs.

8.2.5 Freecad design

8.2.5.1 TYPE OF METAL TO CONSTRUCTION

the construction of the column requires a metal that is resistant to corrosion and consequently the destruction. We can have mentioned some metals such as stainless steel that is the best un this case

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[19] Pilot-plant comparison of Bateman pulsed. (PDF Download Available). Available from: https://www.researchgate.net/publication/292139827_Pilot-plant_comparison_of_Bateman_pulsed_columns_and_mixer_settlers_for_the_extraction_and_stripping_of_zinc_in_the_di2-ethylhexylphosphoric_acid_system [accessed Apr 27 2018].

8.2.5.2 dimension of the extraction column (with rotating discs RDC)

The amount of feed solution that considered as aqueous solution at 90°C (3h) is about 300L(waste +nitric acid ,volume of nitric acid=150 l).

A column of 40 cm radius is suitable in this case.

in most cases found limited to operations where:

- the density differences between the carriers is higher than 50 kg/m^3
- the volumetric phase ratio between dispersed drop phase and continuous

phase is in the magnitude of 0.5 < < 5

- the number of theoretical stages NTS 10

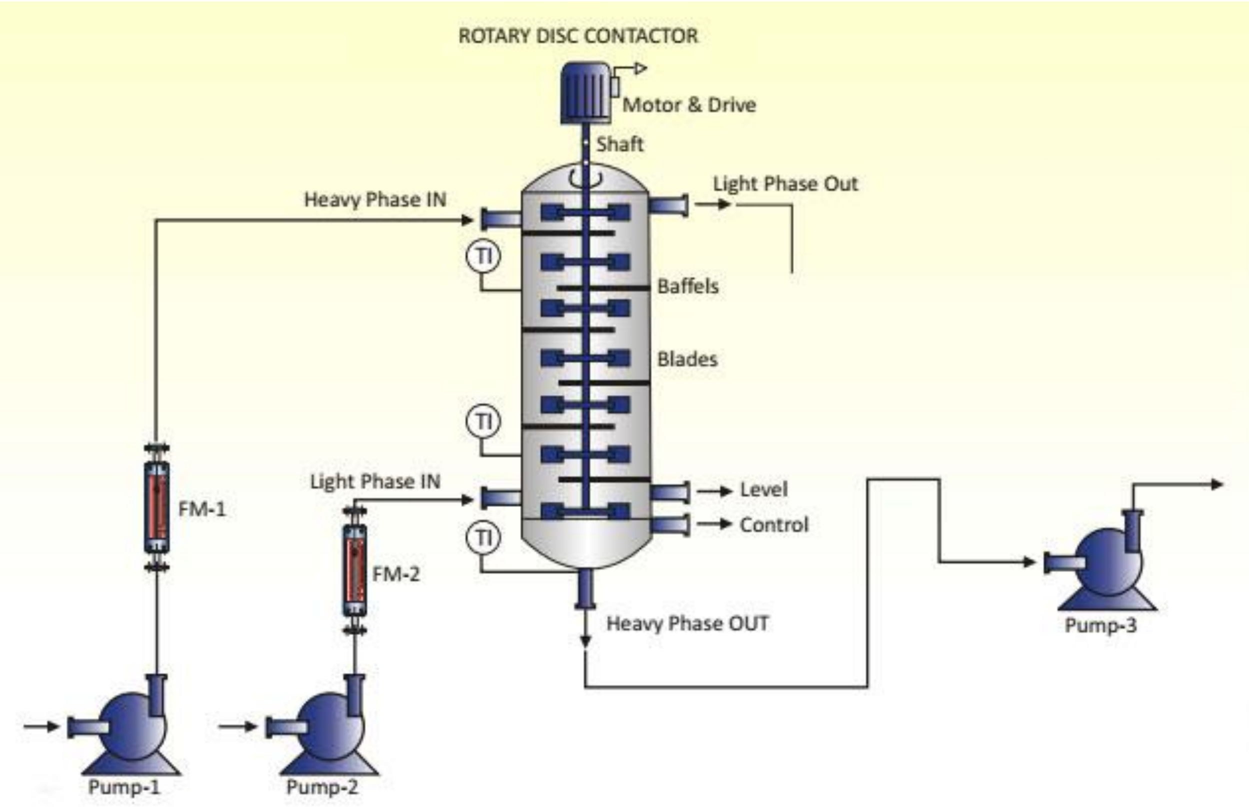


Figure 10 : rotating disc contactor

Equilibrium condition on extraction step is in the range of 8-32%extractant volume percent.

Ashes Recycling Unit

Column	Length (cm)
Height	250
Radius	40
Sheet of stainless steel	2500×125

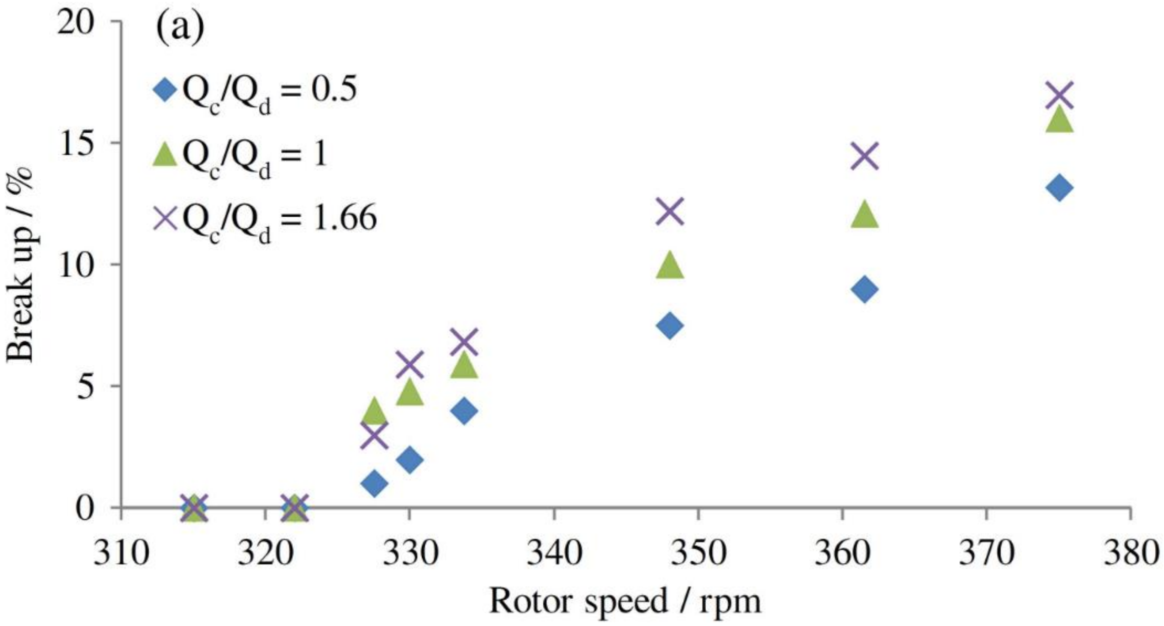
Column height / cm	Column active height / cm	Inner column diameter / cm	Inner stator diameter / cm	Outer rotor diameter / cm	Compartment height / cm	Number of compartment in active region
150	60	9.1	6.1	4.55	3.2	21

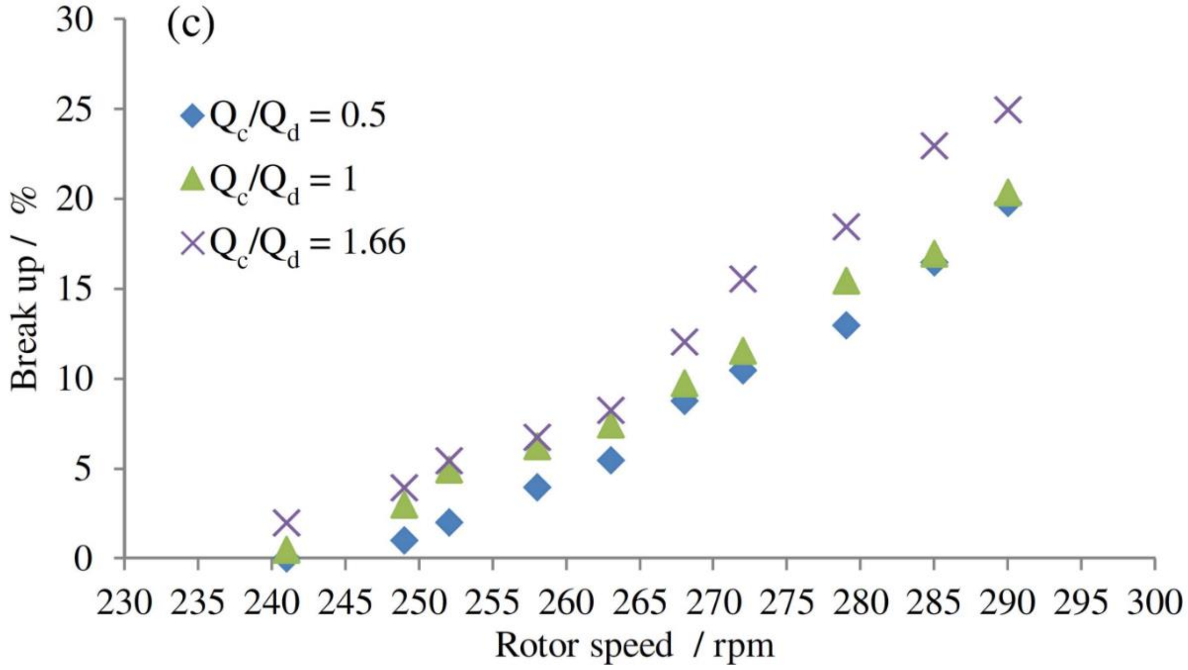
Table 1: Characteristics of the RDC column

8.2.5.3 identification of rotor speed

The first and second critical rotor speeds could also be defined based on breakage probability: the first critical rotor speed for a drop with particular size defines as the rotor speed at which the drop breakage starts. In fact, before the first critical rotor speed, the probability of break up for a drop with specific size is zero. Moreover, the second critical rotor speed (for a drop with a particular size) is a rotor speed at which the probability of breaking that drop is equal to 1

The breakage probabilities versus rotor speed for mentioned chemical systems using glassy nozzles with different inner diameters (1.2 and 2.5 mm) to form various drop sizes by adjusting the Q_c/Q_d ratios and continuous phase heights are presented in next figure regarding to these graphs, the drop breakage increases by increasing the volumetric phase ratio that leads to decrease of the first critical rotor speed. It could be justified with increasing this ratio, the drag forces between the continuous phase and dispersed drops increase results to enhance the probability of drop break up due to collision with the rotors. Mother drop diameter is effective on first critical rotor speed such that the nozzle with larger internal diameter produces larger mother drops with an increase in the probability of break up results to decrement of first critical rotor speed. Increasing the height of continuous phase led to increase of resistance against to upward motion of drops thereupon increment of the break up probability and decrement of the first critical rotor speed. Based on experimental results, the first critical rotor speed for considered chemical system should be 230 rpm.


(a)
◆ $Q_c/Q_d = 0.5$
▲ $Q_c/Q_d = 1$
× $Q_c/Q_d = 1.66$
Break up / %
0
5
10
15
20
310
320
330
340
350
360
370
380
Rotor speed / rpm


(c)
◆ $Q_c/Q_d = 0.5$
▲ $Q_c/Q_d = 1$
× $Q_c/Q_d = 1.66$
Break up / %
0
5
10
15
20
25
30
230
235
240
245
250
255
260
265
270
275
280
285
290
295
300
Rotor speed / rpm

8.2.5.4 Characteristics of LIX® 984N

Typical properties Physical and performance specifications

Specific gravity	(25 °/25 °C) 0.935 – 0.955 g/cm³
Flash point	Greater than 170 °F=76 °C
Copper complex solubility	> 30 g/l Cu at 25 °
Maximum copper loading	≥ 5.1 g/l Cu
Extraction isotherm point	≥ 4.40 g/l Cu
Extraction kinetics	≥ 95 % (30 seconds)
Extraction Cu/Fe selectivity	≥ 2000
Extraction phase separation	≤ 70 seconds
Strip isotherm point	≤ 1.8 g/l Cu
Net copper transfer	≥ 2.70 g/l Cu
Strip kinetics	≥ 95 % (30 seconds)
Strip phase separation	≤ 80 seconds

Table 2: Typical properties physical and performance specifications

materials	Density (kg/m³)
Copper	999
Nitric acid	1510
Oxime LIX	806

Table 3 :Density of solutions

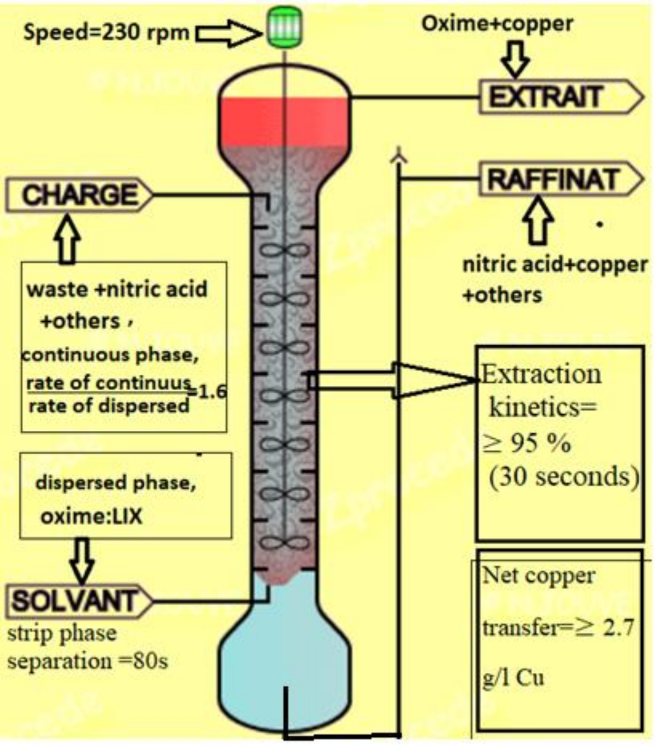


Figure 11 :input and output of column;

Solvent = light phase (feed at bottom), Solvent = dispersed phase (top interface)

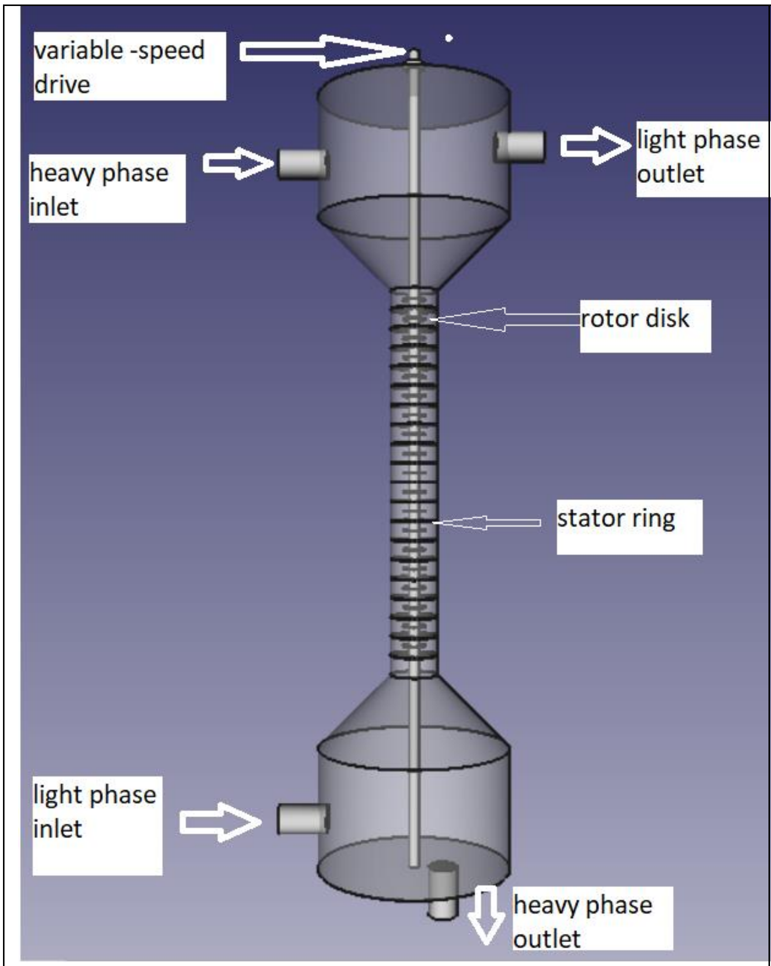
To complete 95% of the extraction process ,it takes 30 seconds ,in others words of the solute (copper) passes from solution A(waste + nitric acid) to solvent . the stripping of copper takes 80 seconds.

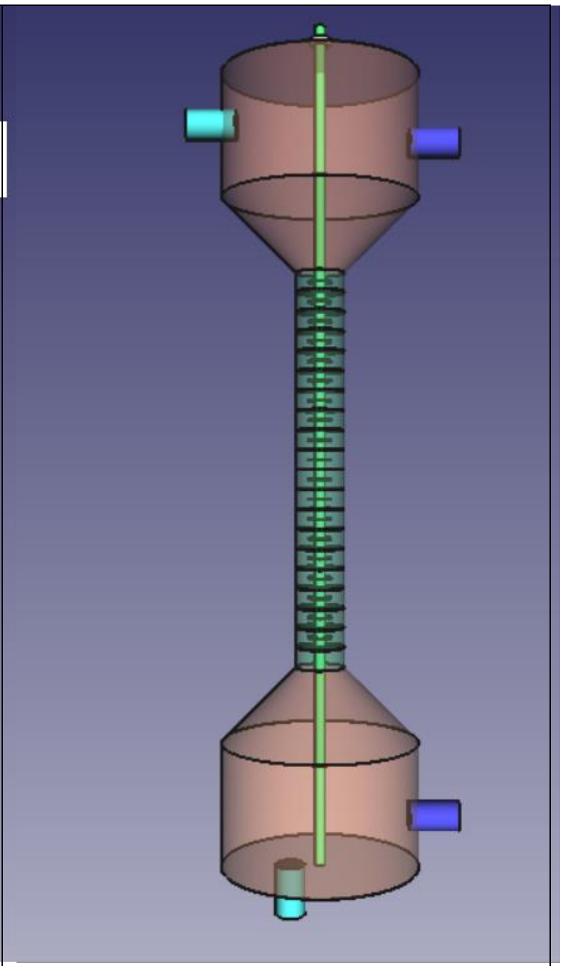
Parts	Dimension
Covering column	Internal diameter:212 mm Outside diameter:220mm
Columns that carry stators	Number:3 Diameter:4 mm Height 2500 mm
Stator	Number:10 Internal diameter:120 mm outside diameter:204 mm Height:15 mm Spaced:150 mm
Decanter	Number :2

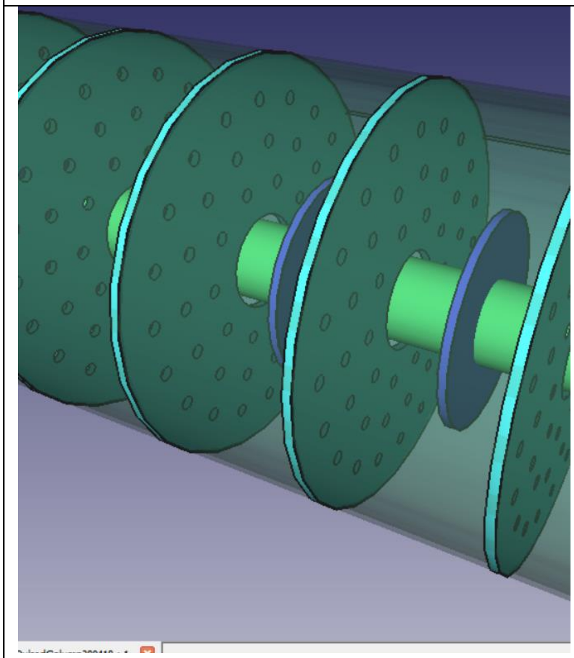
(cylinder+cone)	Radius 1:110 mm Radius 2:200 mm Height: 100 mm -Cylinder: Height :300 mm Diameter:400 mm
Rotation axis	Diameter :40 mm, height:3500 mm
Rotor perforated(20 punch ,D=8 mm)	Number :10 Internal diameter:40 mm Outside diameter:100 mm Height:15 mm Spaced :150 mm

Table 4: dimensions of parts of columns

8.2.5.5 Bateman pulsed column







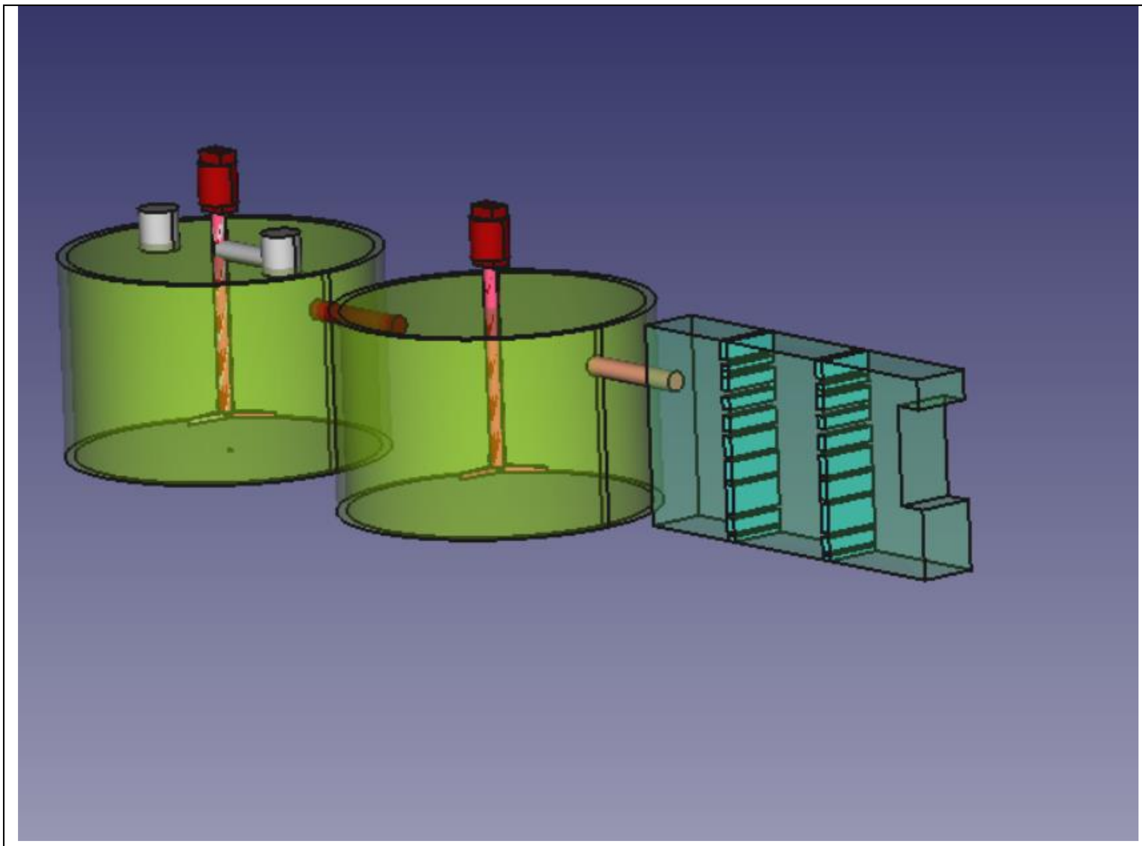
BatemanPulsedColumn100518.FCStd

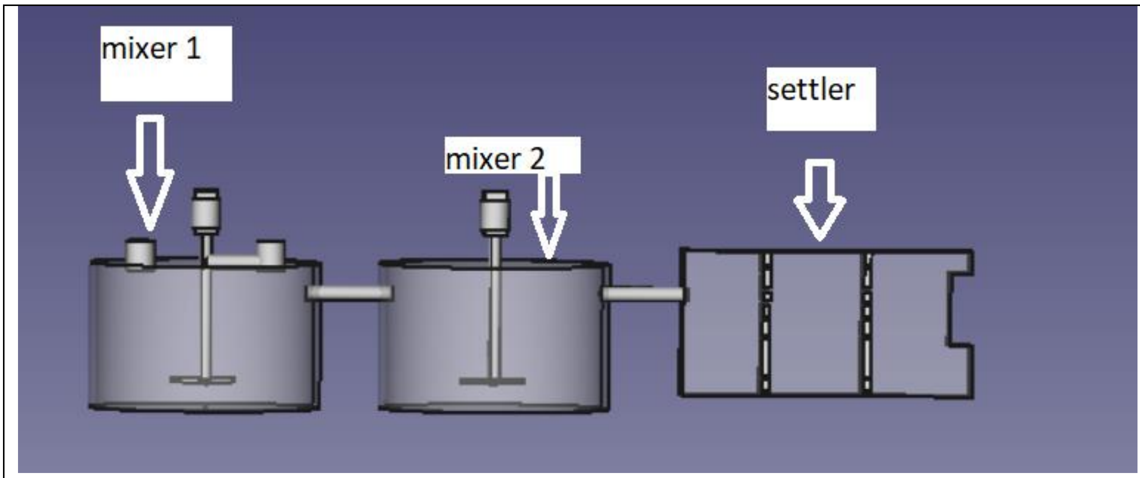
Dimensions of Bateman pulsed column

materials	radius (m)	Height (m)	number
Stator ring	0.245	0.01	19
rotor disk	0.125	0.02	19
Main tube	0.25	4	1
Tube (driver)	0.05	8.5	1
Inlet & outlet	0.15	0.5	2

Total surface needed to bateman pulsed column =20.4 m^2 (11 sheets 1×2 m)

8.2.5.6 Mixer settler





Mixer-settler_schema-030518.FCStd

Dimensions of Mixer –settler

Component	Height(m)	Radius (m)
Mixer 1	1	0.75
Inlet 1	0.2	0.1
inlet 2	0.2	0.1
Outlet 1	0.6	0.05
Mixer 2	1	0.75
Inlet 1	0.2	0.1
inlet 2	0.2	0.1
Outlet 1	0.6	0.05

Component	Length (m)	width (m)	Height (m)
settler	2	0.3	1
Barrier to scroll	2	0.3	2

Total surface needed to mixer=21.2 m^2

Total surface needed to settler=6.3 m^2

Total surface = 27.45 m^2 (13 sheet 1m×2 m)

8.2.5.7 RDC column

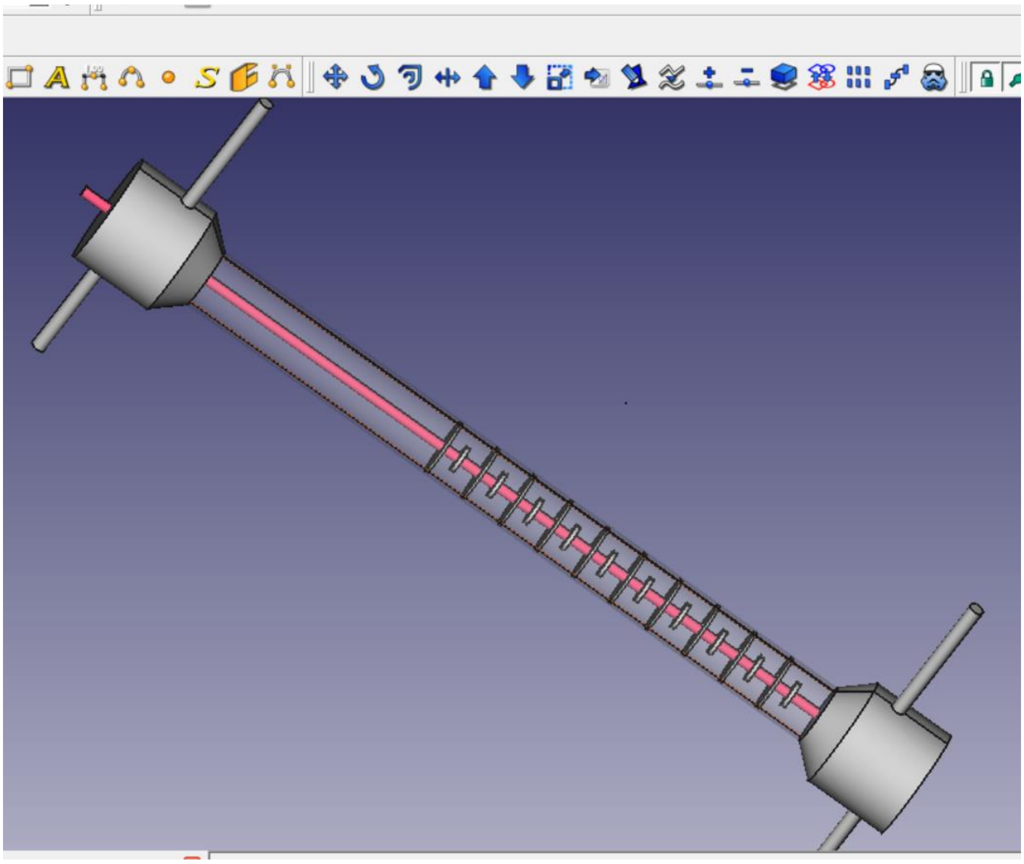


Figure 12 : overview of RDC column

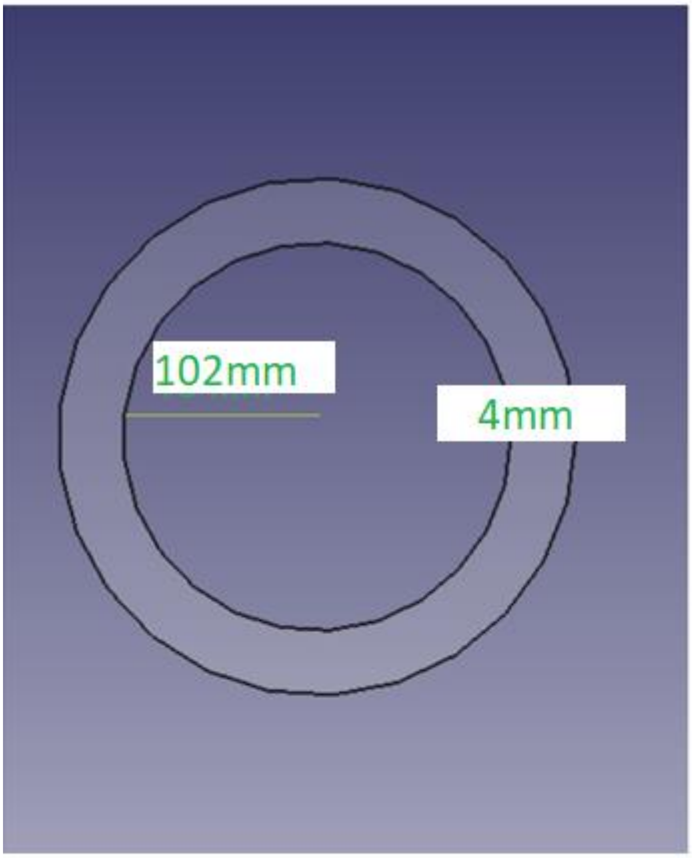


Figure 13 : top and side face of column

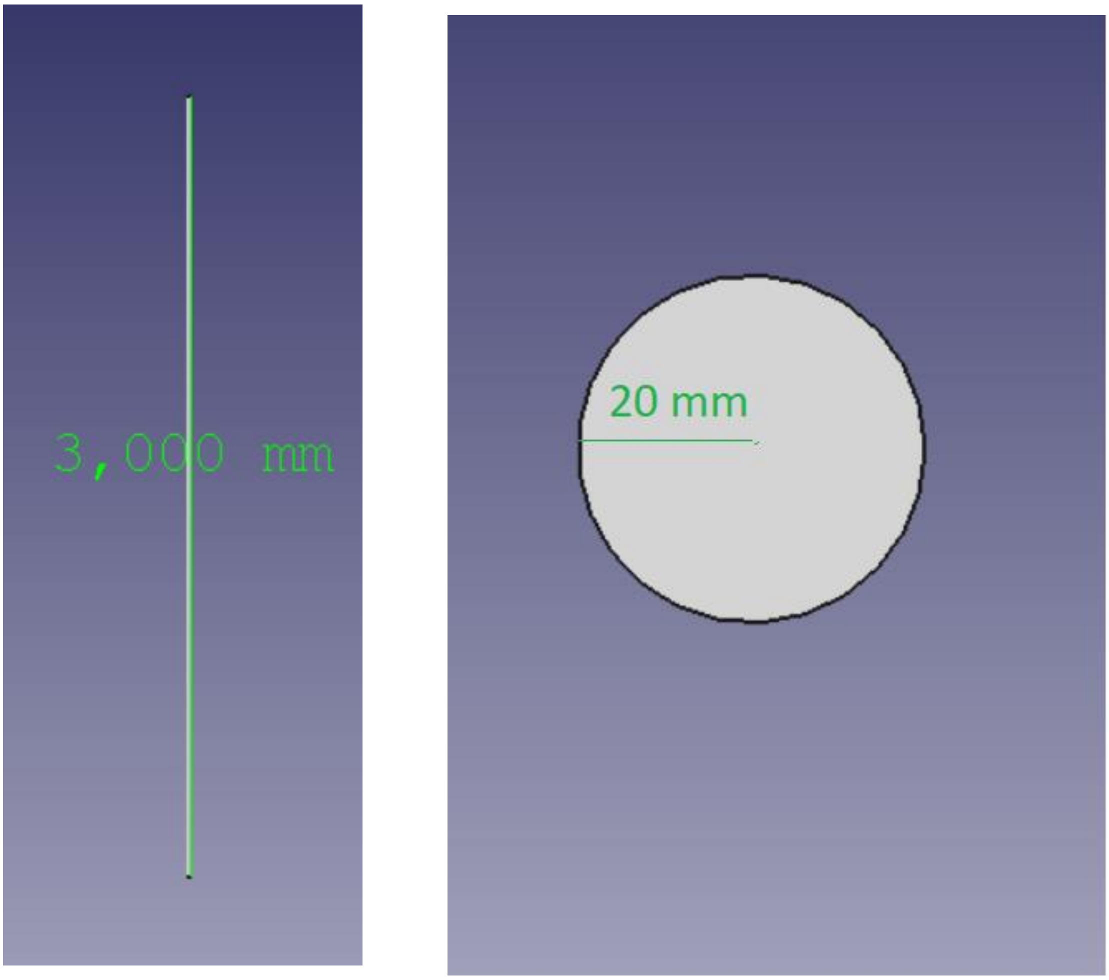


Figure 14 : rotation axis

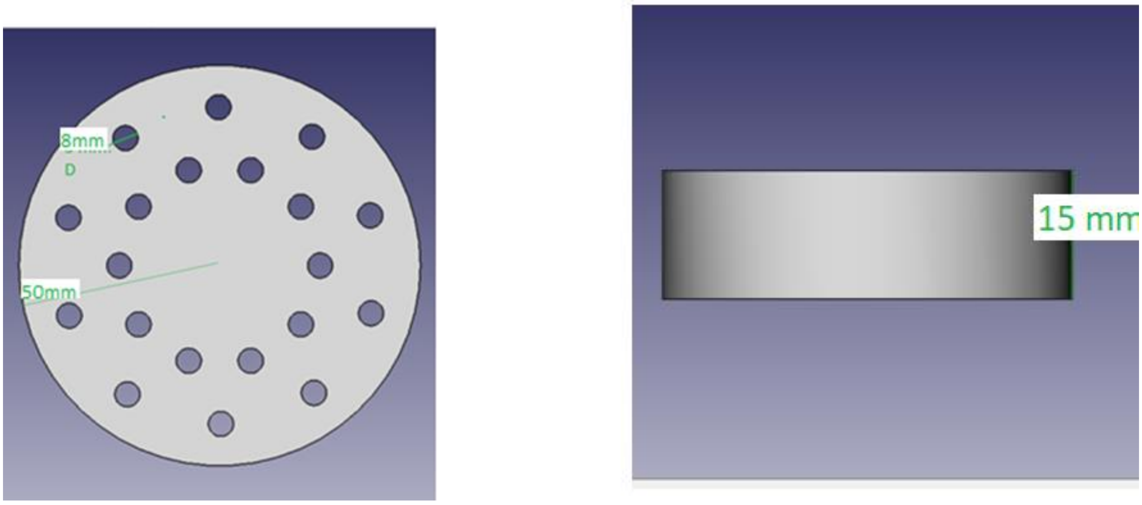


Figure 15 : rotor perforted (20 perforation,)

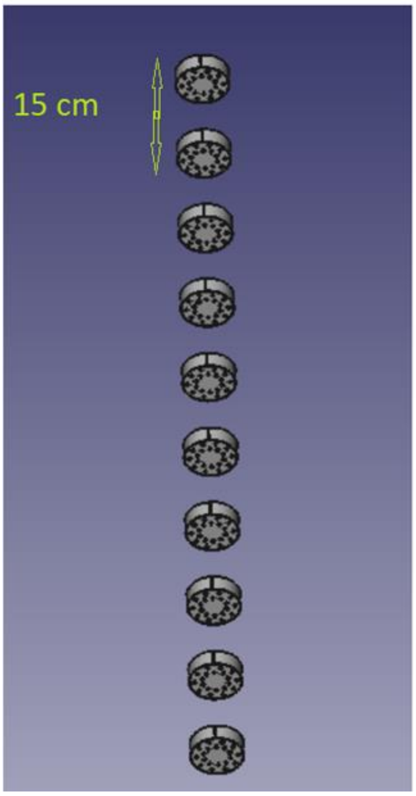


Figure 16 : 10 rotor spaced 15 cm

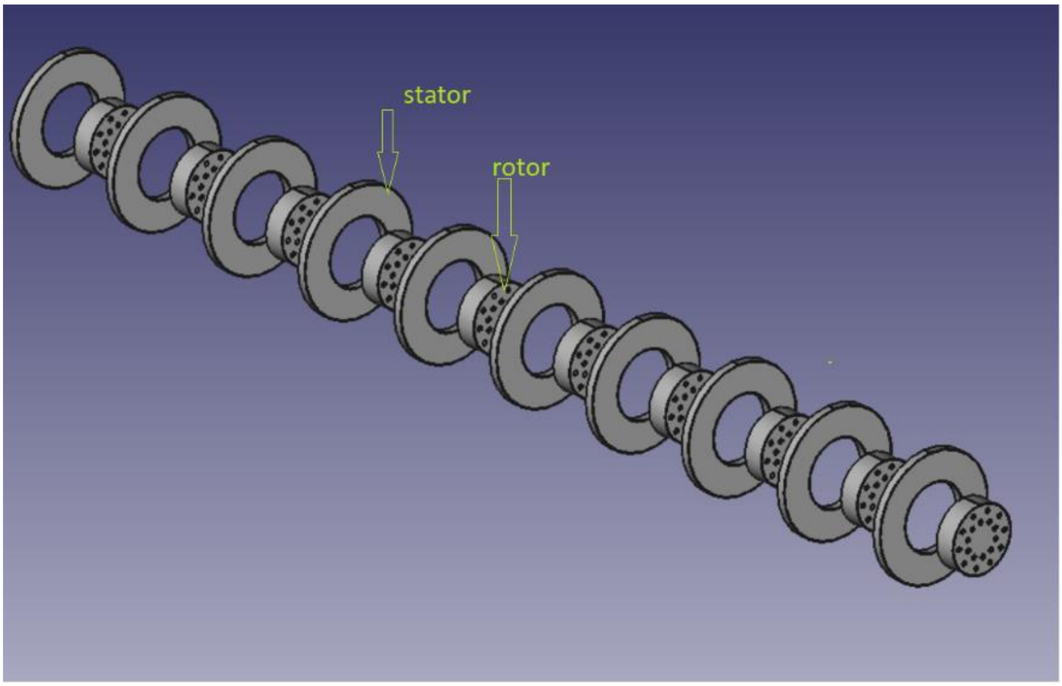


Figure 17 : stator (10 pieces) with rotor

Figure 18 :Distribution of rotors and stators

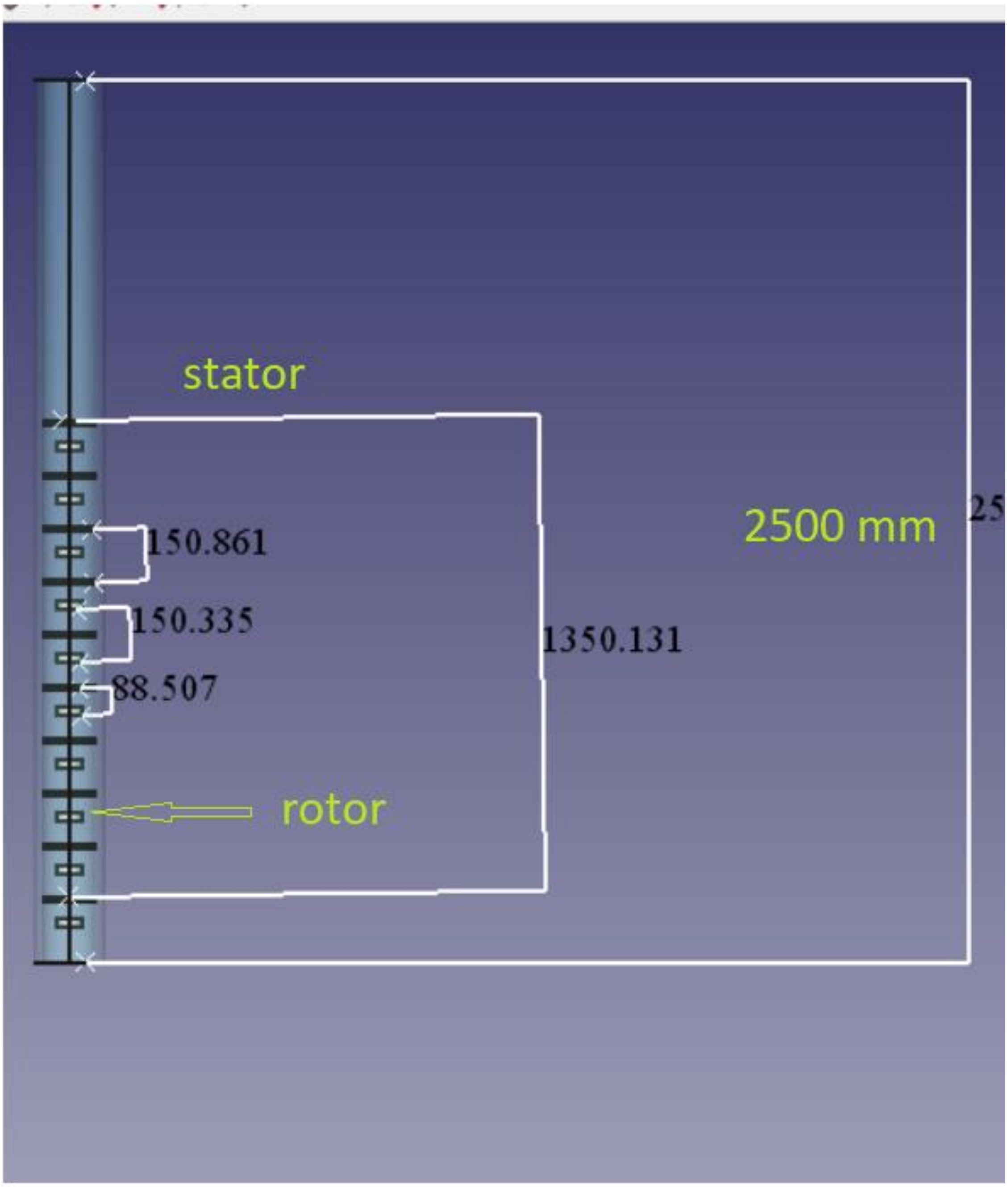
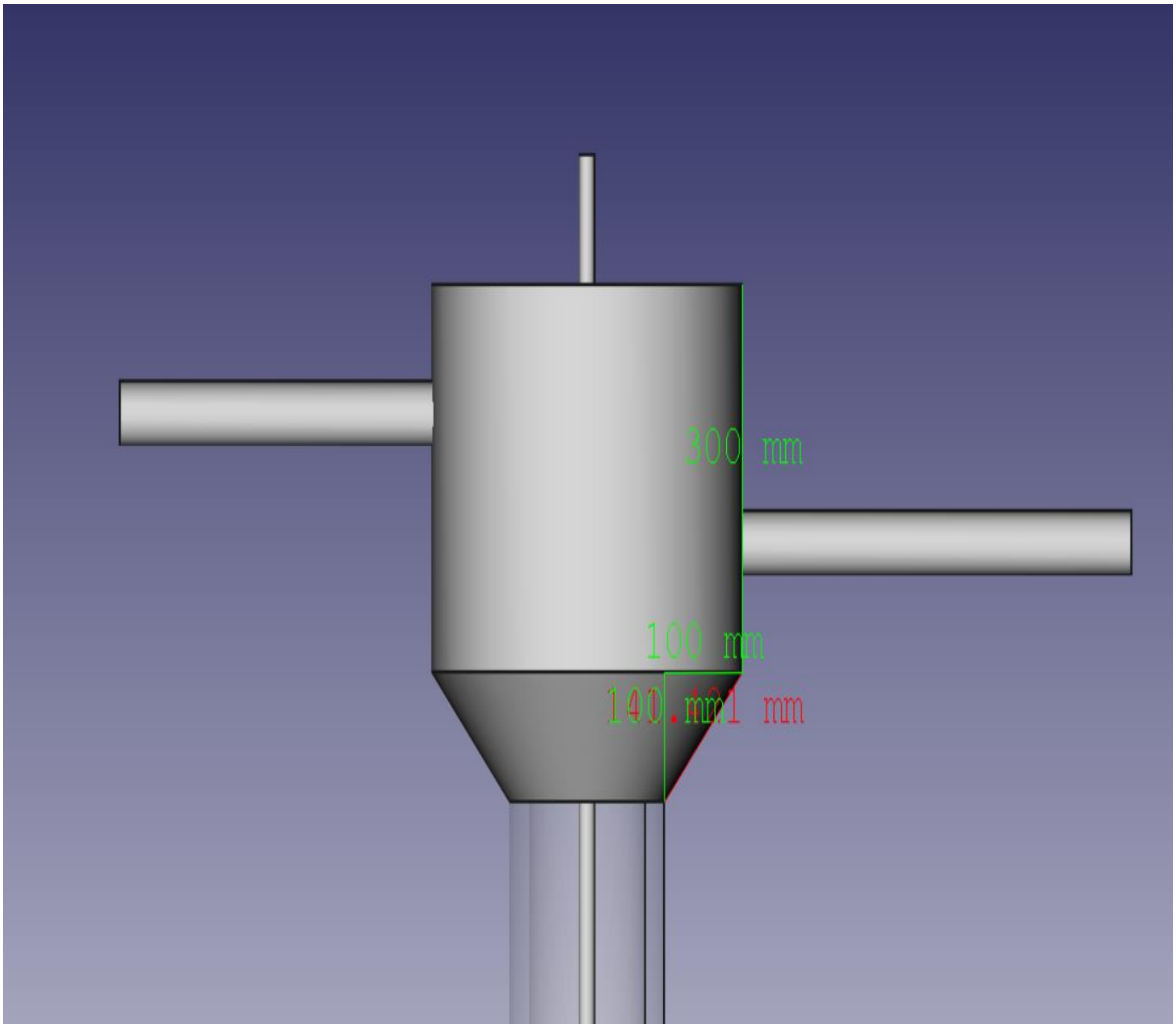


Figure 19 :Distribution of rotors and stators


300 mm
100 mm
140 mm
140.401 mm

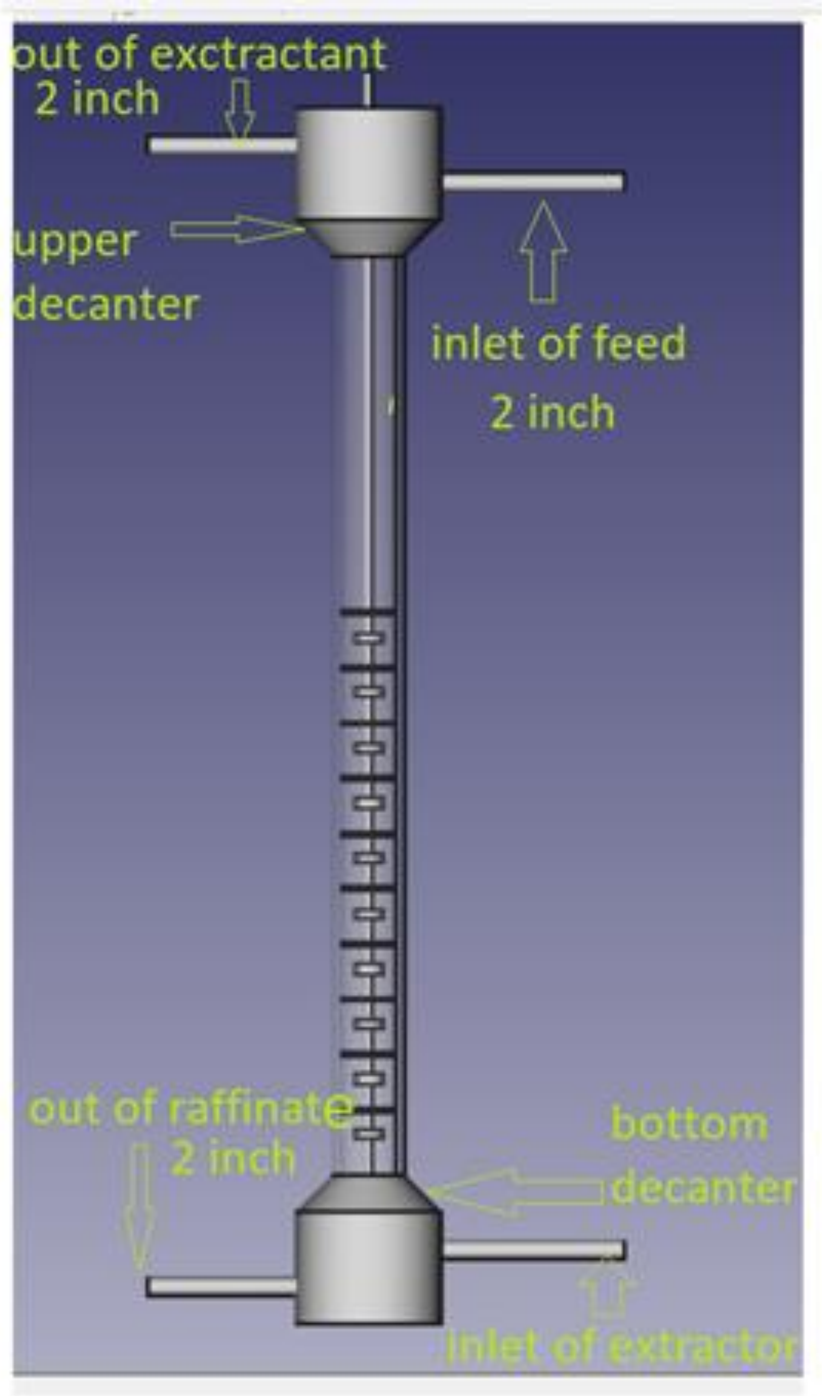


Figure 20 :upper and bottom decanter (200 mm of radius, height 300 mm

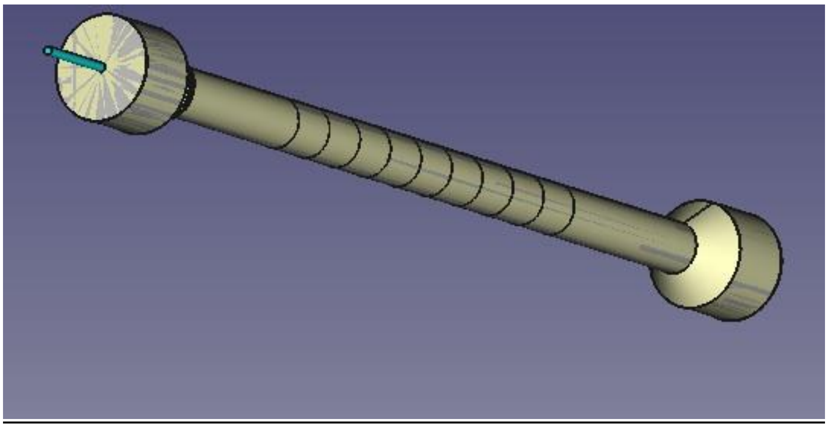
Cone r1=200mm, height 100 mm)

Ashes Recycling Unit

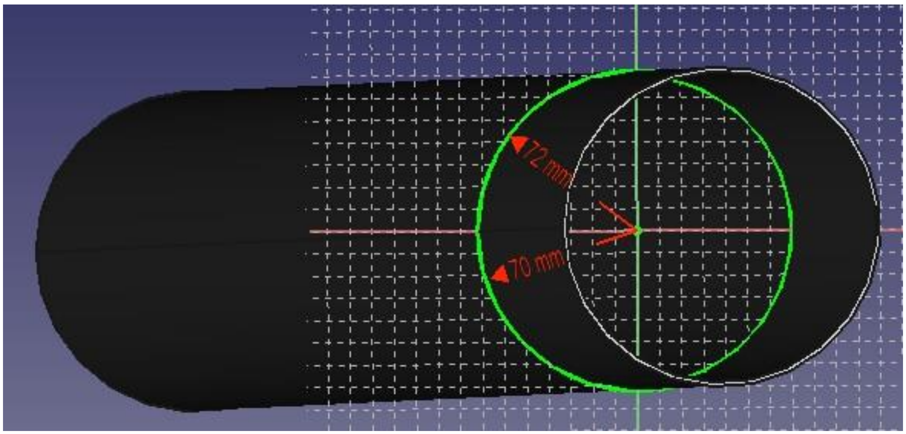
parts	Freecad files
Column	column06082018.FCStd
Rotation axis	column wih rotation axis140818.FCStd
Stator	stator 06082018.FCStd
rotor	rotor 06082018.FCStd
System	FINAL DESIGN OF COLUMN140818.FCStd

Table 5 :list of parts that formed a system of extraction

8.2.5.8 The Coulumn:

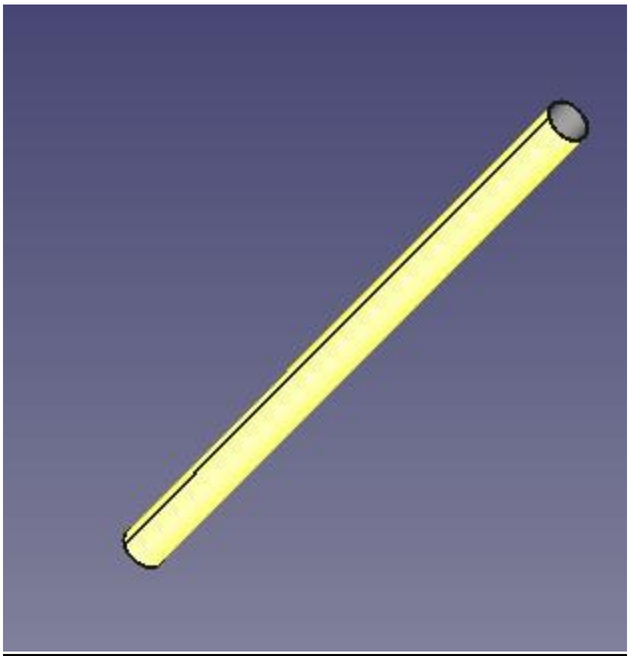


total height: 310 cm

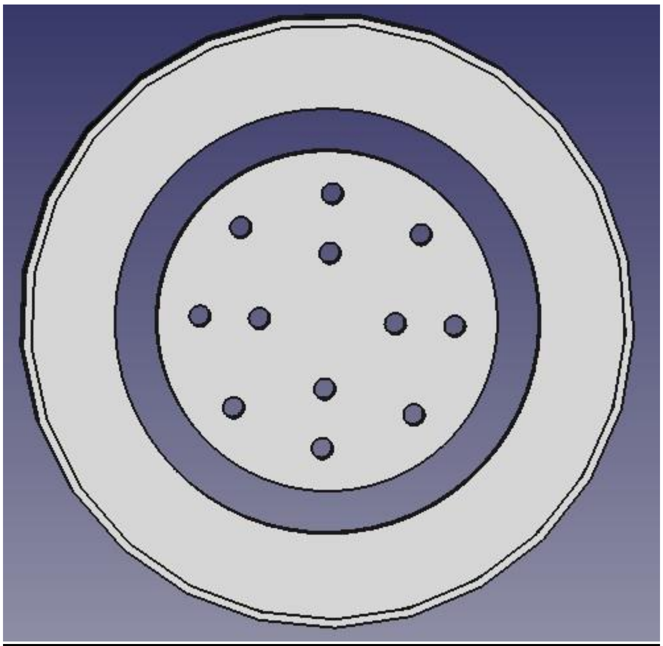


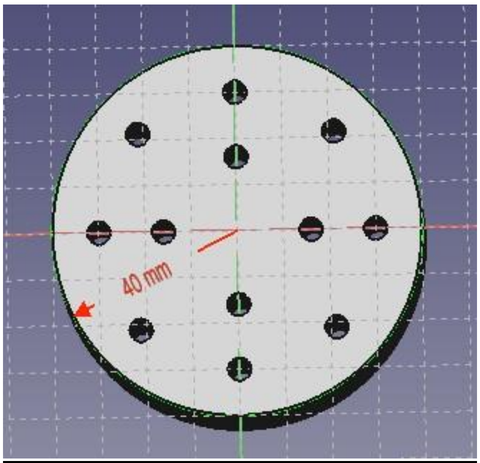
Diameter: 14 cm

Ashes Recycling Unit

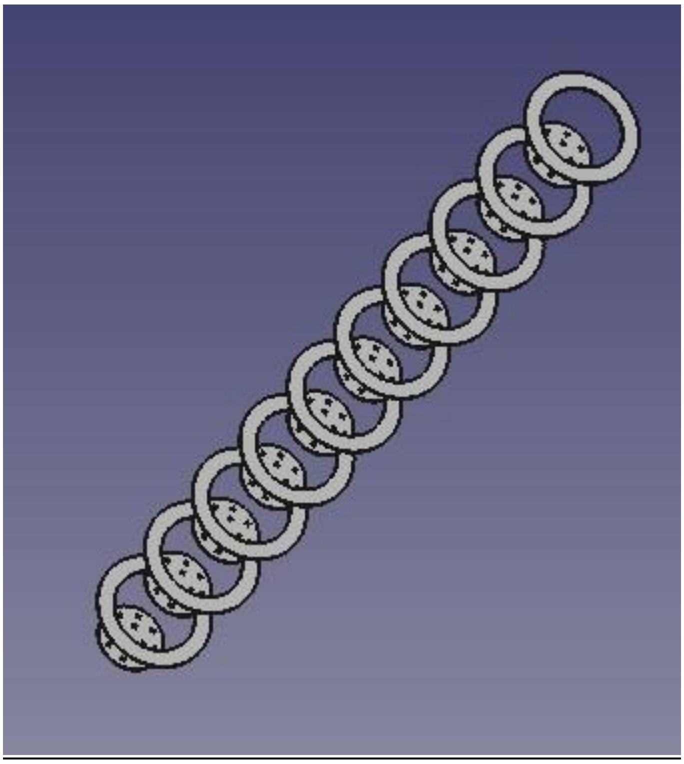


height: 250 cm



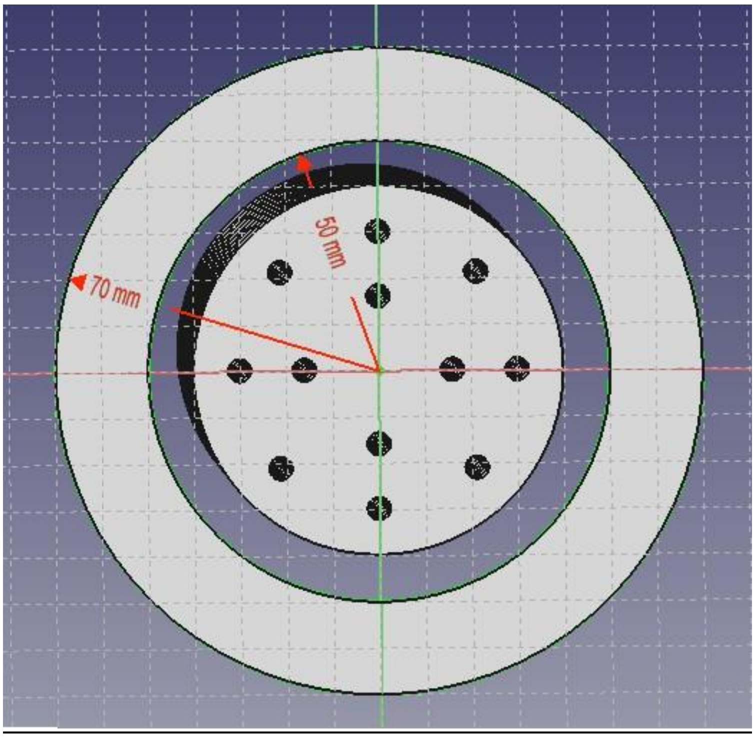


Diameter: 8 cm



thickness: 2 mm

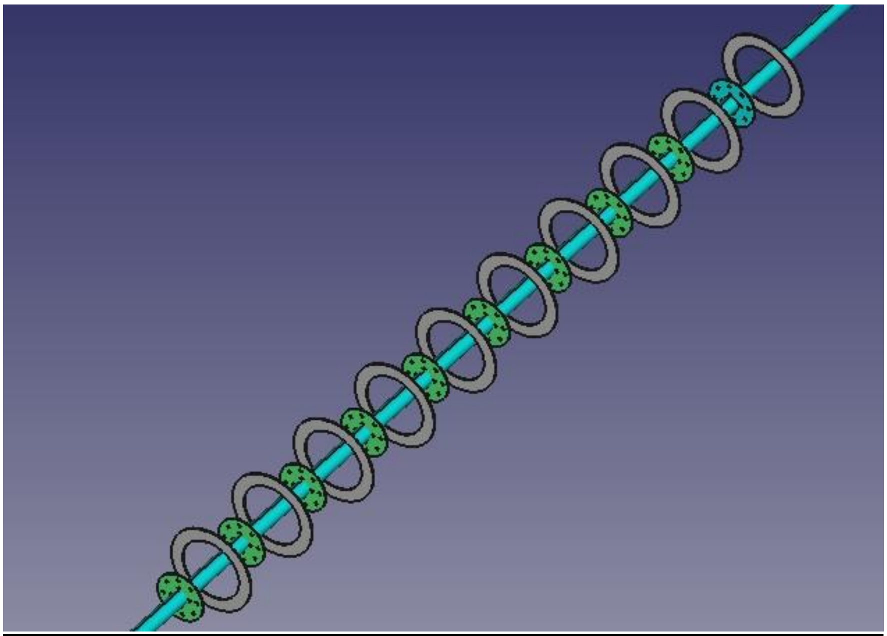
number of disques: 10

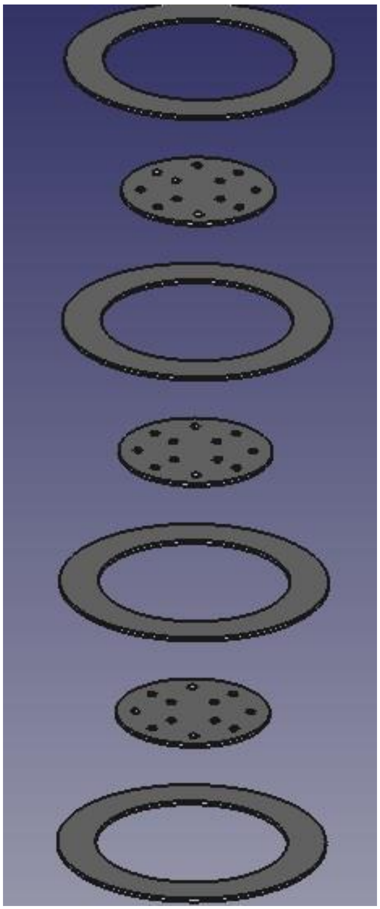


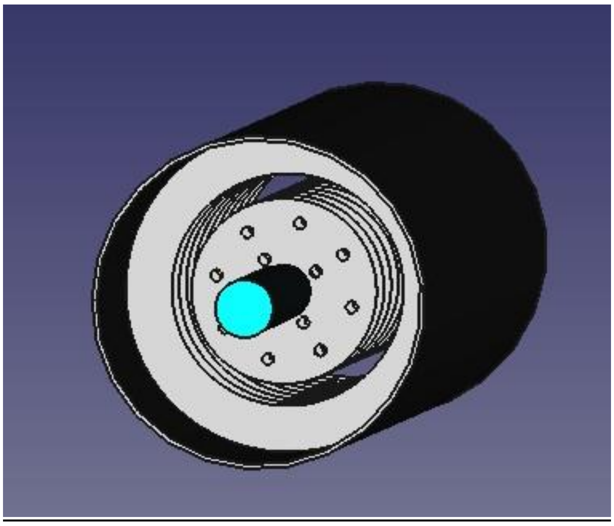
diameter 1 : 10 cm

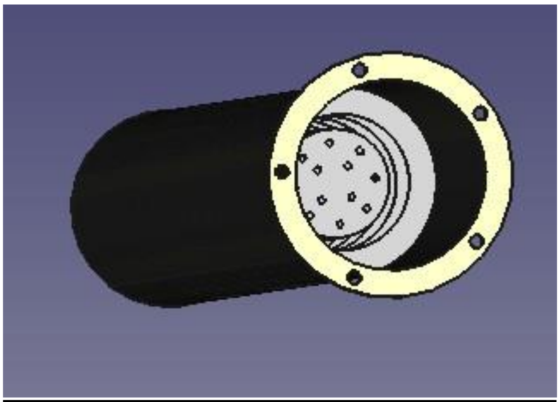
diameter 2 : 14 cm

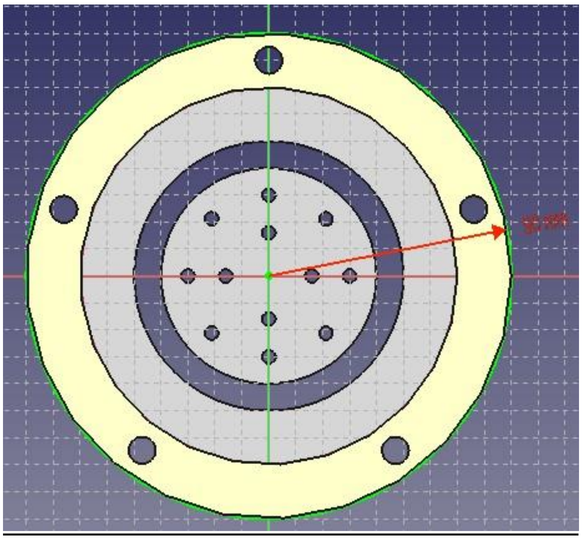
axe: height: 350 cm



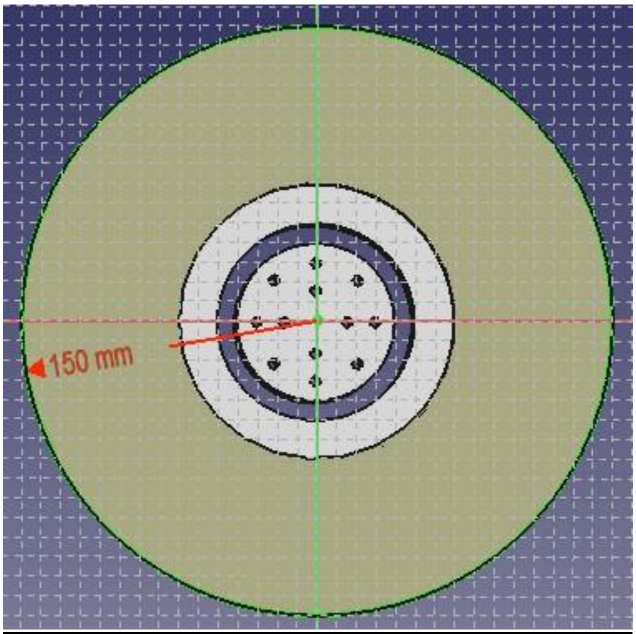


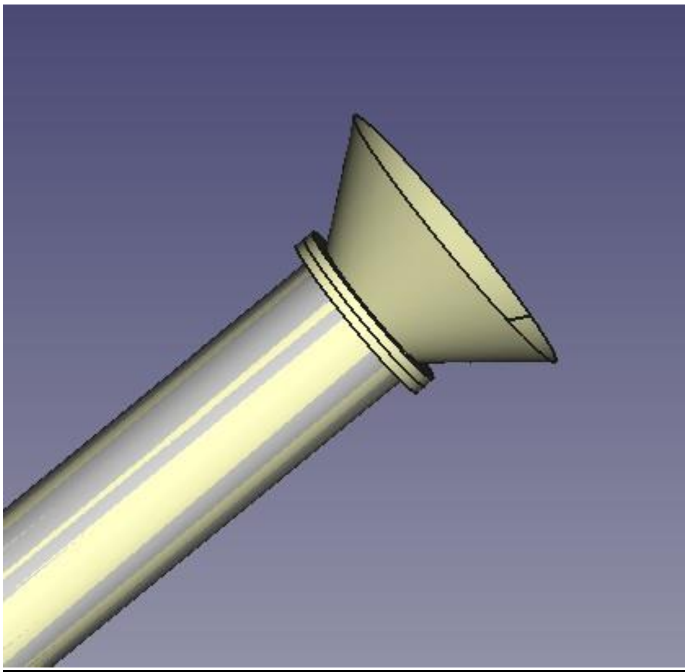






diameter: 18 cm

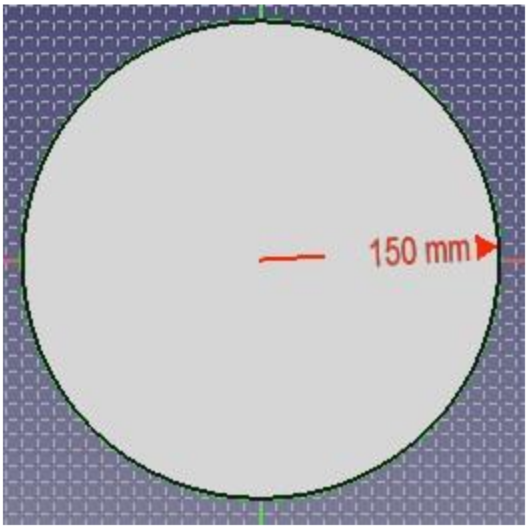




diameter 1 ; 14 cm

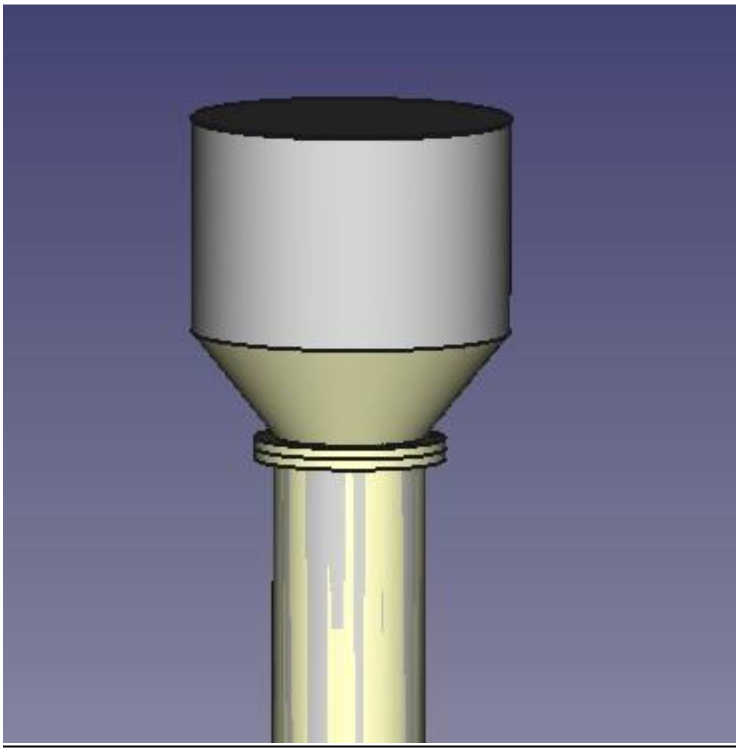
diameter 2 : 30 cm

height: 10 c m



diameter: 30 cm

height : 20 cm



thickness:2mm

Manufacturing

Ashes Recycling Unit

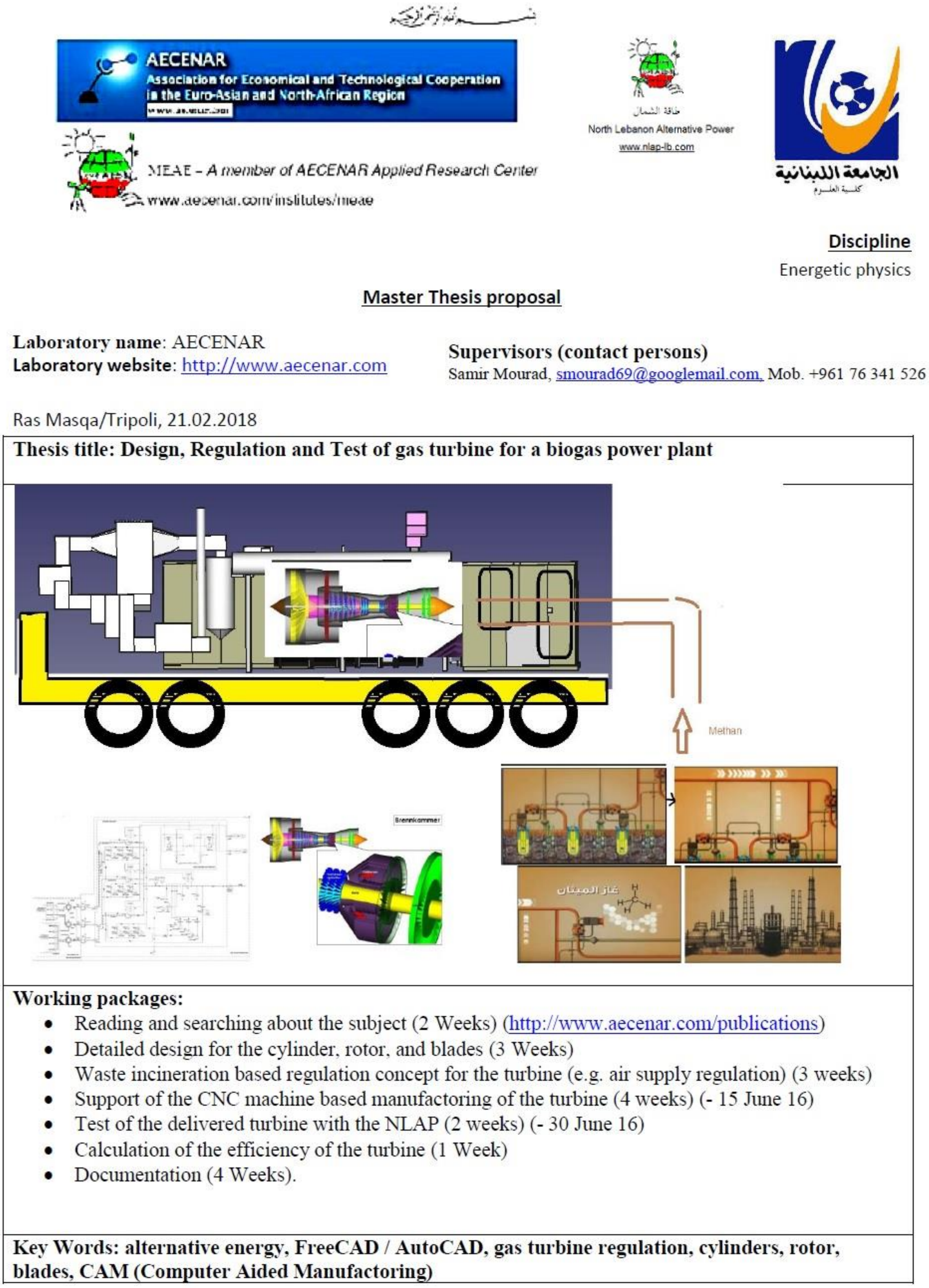
Ashes Recycling Unit


F204
UC204

Ashes Recycling Unit

9 Gas Turbine Test rig

9.1 Specification



بسم الله الرحمن الرحيم

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كلية العلوم

Discipline
Energetic physics

Master Thesis proposal

Laboratory name: AECENAR
Laboratory website: http://www.aecenar.com

Supervisors (contact persons)
Samir Mourad, smourad69@googlemail.com, Mob. +961 76 341 526

Ras Masqa/Tripoli, 21.02.2018

Thesis title: Design, Regulation and Test of gas turbine for a biogas power plant

Working packages:

- Reading and searching about the subject (2 Weeks) (http://www.aecenar.com/publications)
- Detailed design for the cylinder, rotor, and blades (3 Weeks)
- Waste incineration based regulation concept for the turbine (e.g. air supply regulation) (3 weeks)
- Support of the CNC machine based manufactoring of the turbine (4 weeks) (- 15 June 16)
- Test of the delivered turbine with the NLAP (2 weeks) (- 30 June 16)
- Calculation of the efficiency of the turbine (1 Week)
- Documentation (4 Weeks).

Key Words: alternative energy, FreeCAD / AutoCAD, gas turbine regulation, cylinders, rotor, blades, CAM (Computer Aided Manufactoring)

10 Fuel (H2/Methan) Burner Unit

10.1 Specification

10.1.1 Requirements

Gas pressurized tanks

cooled burning chamber with fuel chain

(15 kg/s cooling throughput)

10.1.2 Working Packages / Timeplan

10.2 System Design

Fuel Burner

A burner is the mechanical element that ensures the production of heat by mixing a fuel (gaseous, liquid or solid) with an oxidant (usually air, naturally containing oxygen), thus producing a combustion . The mixture requires the best adjustment so that the combustion efficiency is maximum and that the combustion is the best possible, that is to say, generating as little as possible of unburnt and pollutants.

Fuel (H2/Methan) Burner Unit

large natural gas burner.

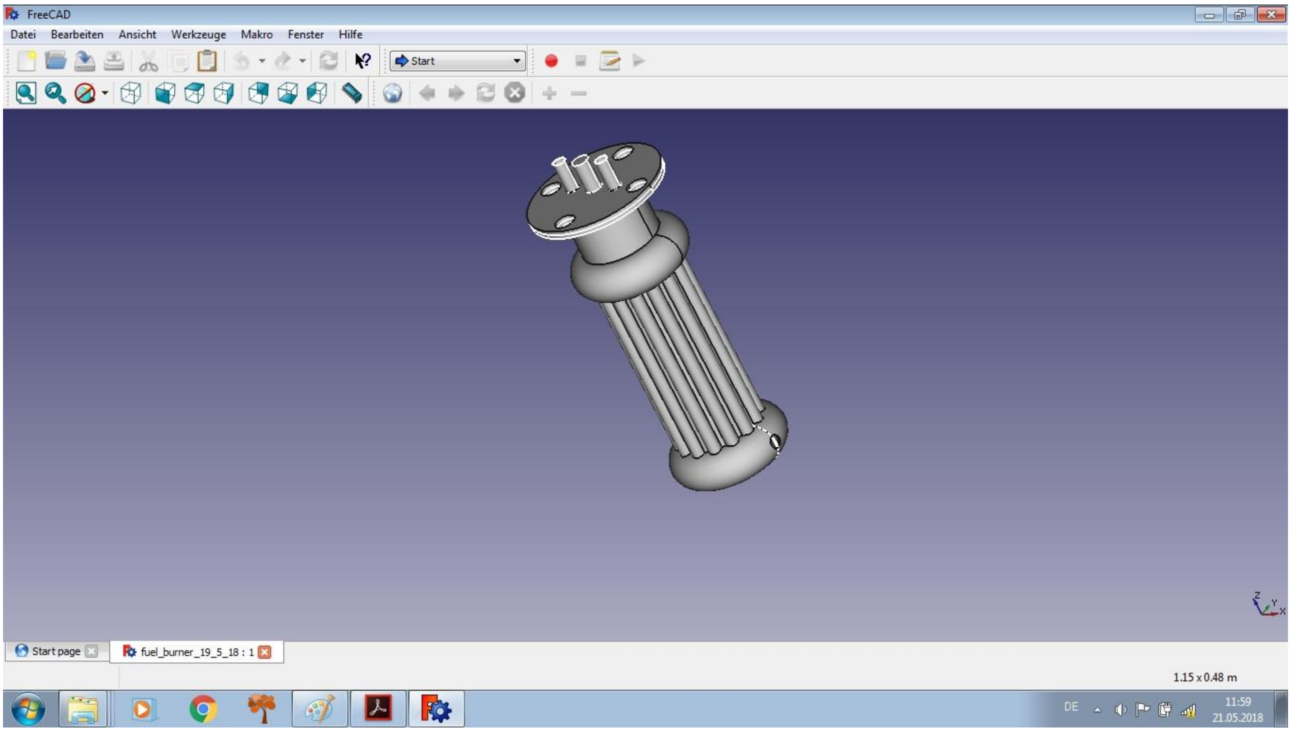
Burner with natural gas equipping an industrial cooking oven.

Combustion fan with frequency variator for gas / oil burners.

The fuel supplying a burner may be gaseous, liquid or solid, alone or as a mixture, for example:

- dihydrogen
- methane (natural gas);
- butane;
- propane ;
- fuel oil;
- oil (fossil, plant, animal);

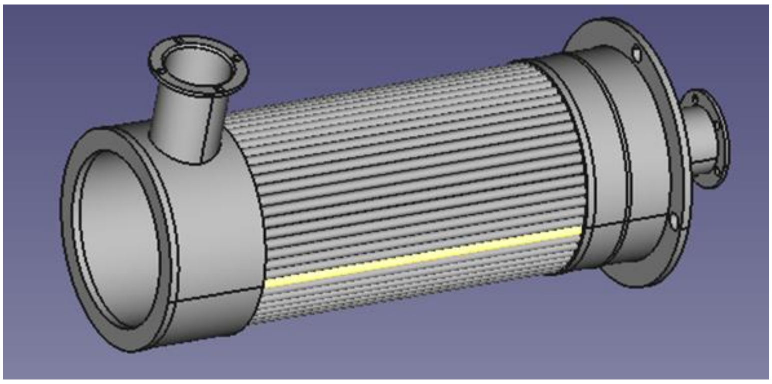
- pulverized coal;
- wood pellets and crushed biomass waste;
- waste (in cement burners for example).



fuel_burner_19_5_18.FCStd

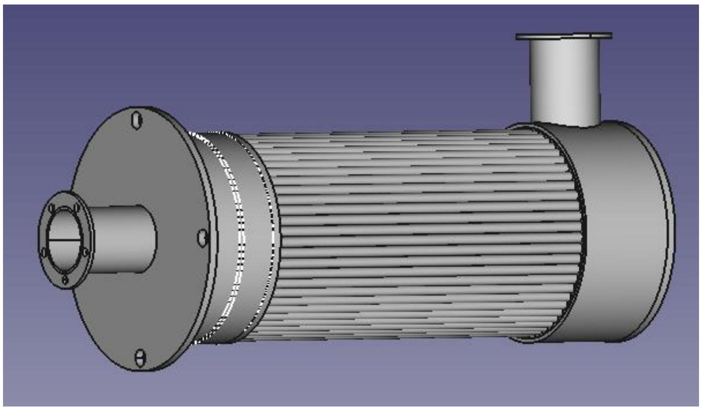
Fuel (H2/Methan) Burner Unit

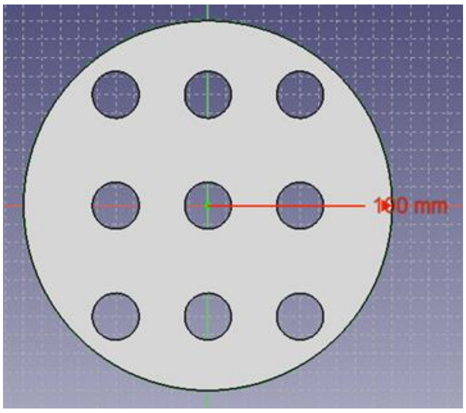
Design 1

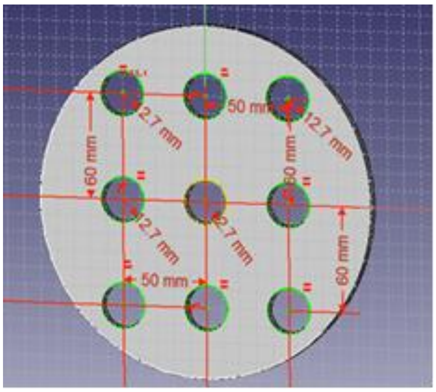


Diameter : 20 cm

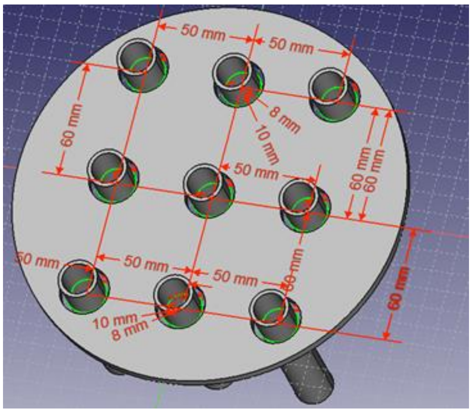
Thickness: 5 mm

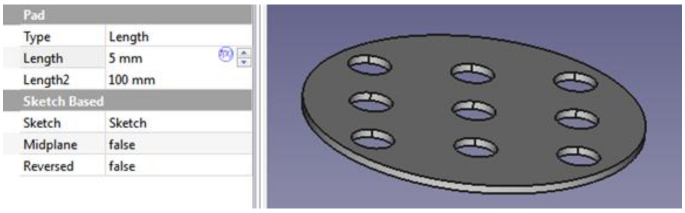






Fuel (H2/Methan) Burner Unit

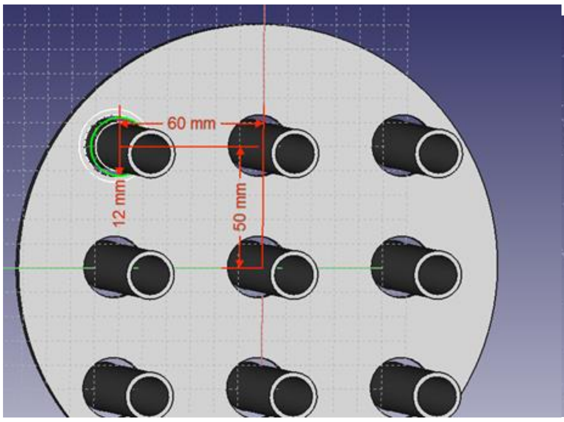


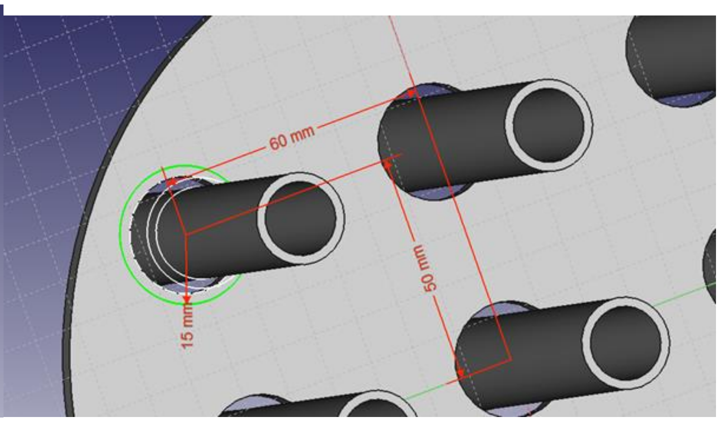


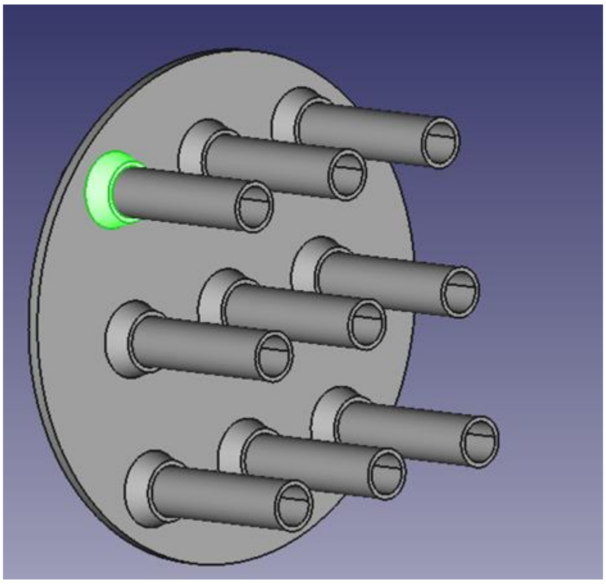
Pad	
Type	Length
Length	5 mm
Length2	100 mm
Sketch Based	
Sketch	Sketch
Midplane	false
Reversed	false

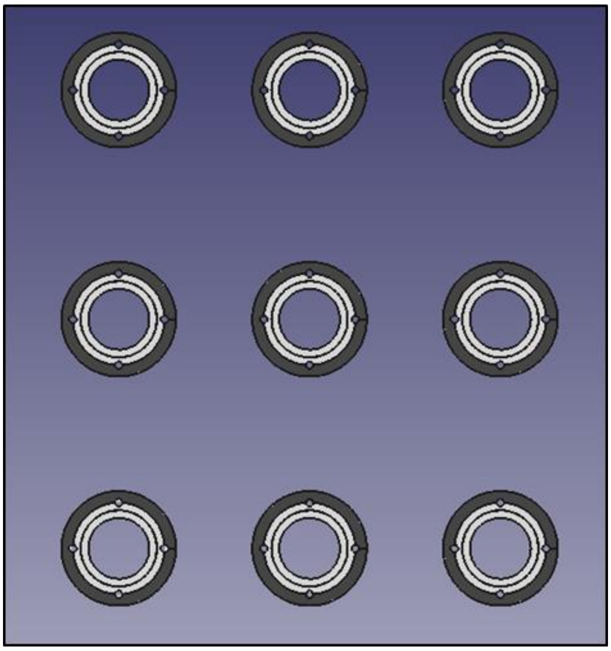
length 1: 2cm

length 2: 8 cm







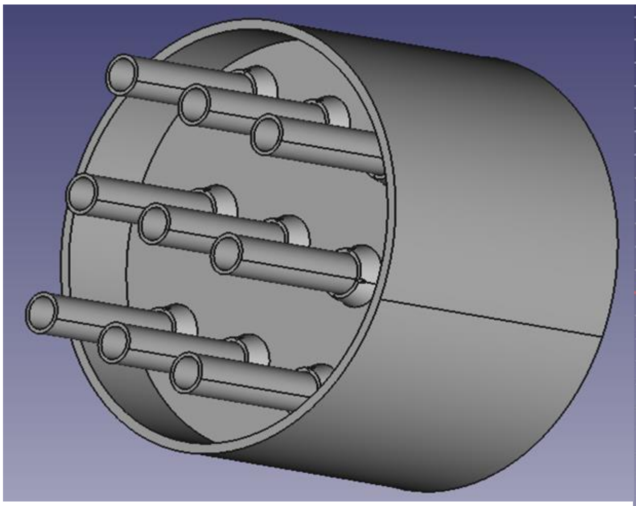


length of cone : 1 cm

Nb of hole : 4

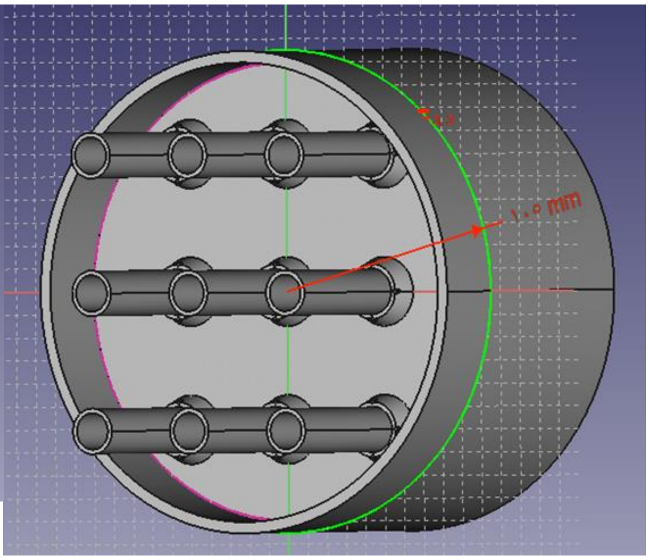
Diameter of hole: 2mm

Fuel (H2/Methan) Burner Unit



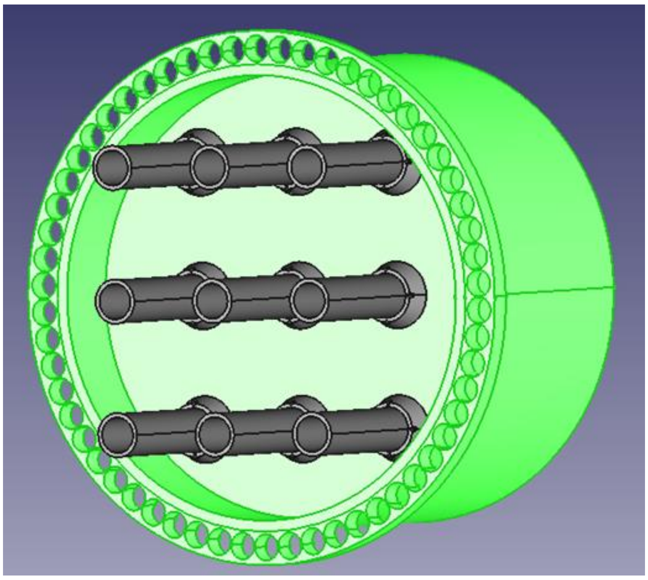
Length 1: 3.5 cm

Length 2 : 10 cm



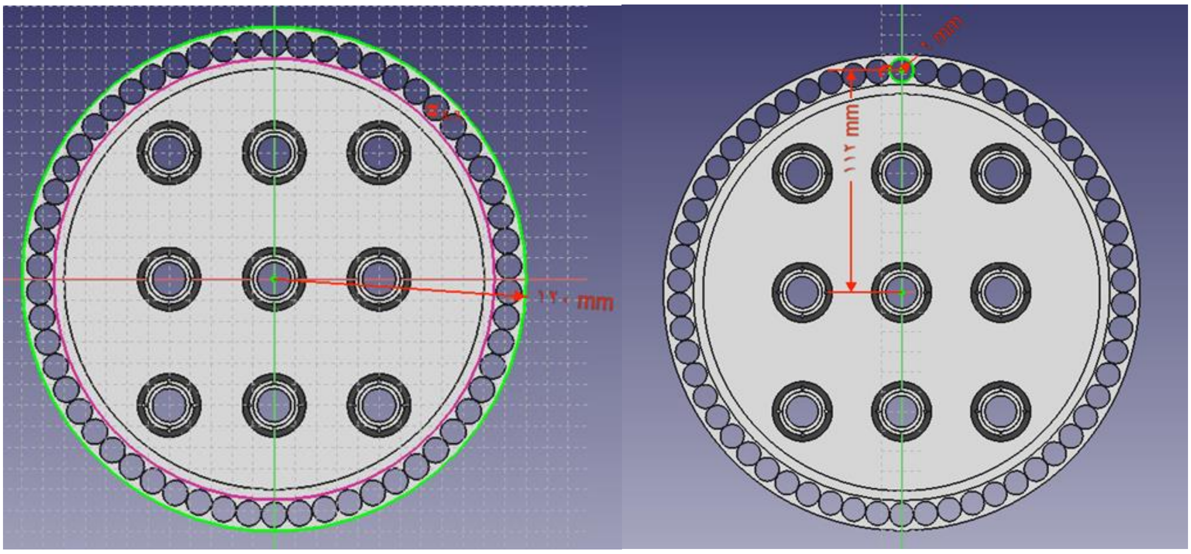
Ext diameter : 21 cm

Int diameter : 20 cm



Thickness : 1cm

Fuel (H2/Methan) Burner Unit

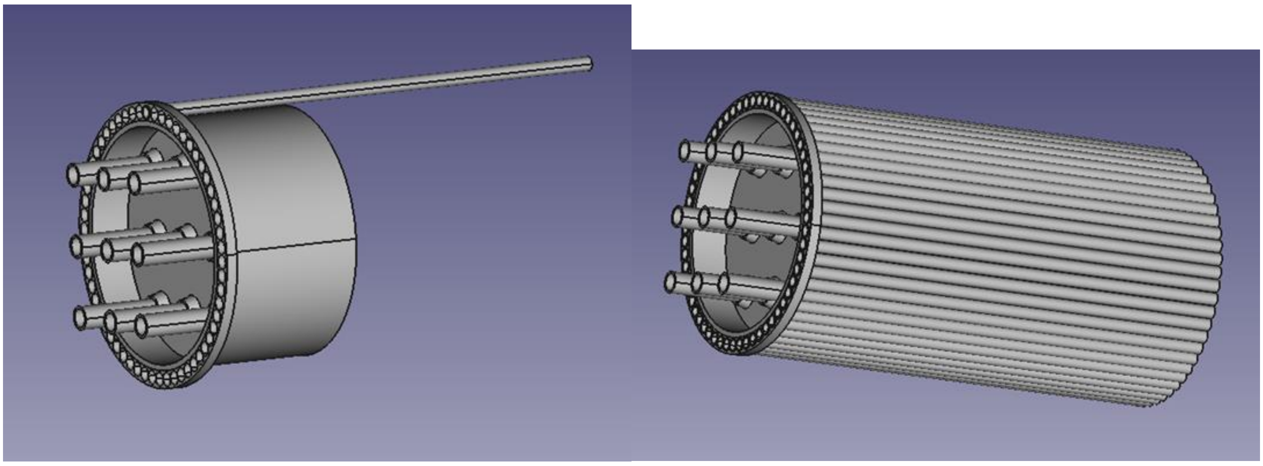


Diameter of hole : 12 mm,

Nb of hole: 58

Int diameter: 21 cm

Ext diameter: 24 cm



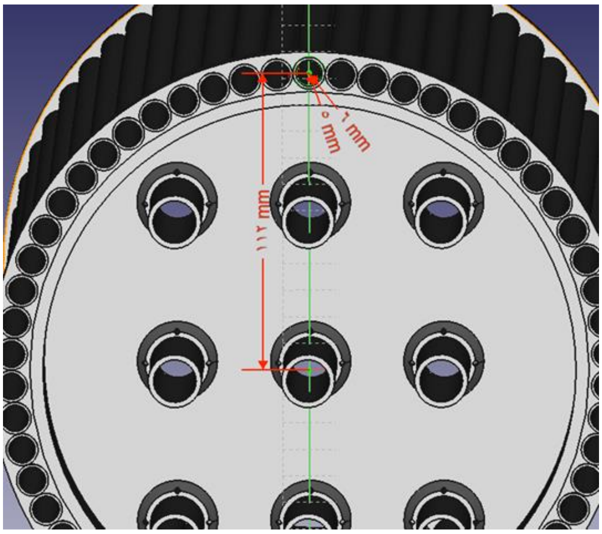
Length : 43 cn

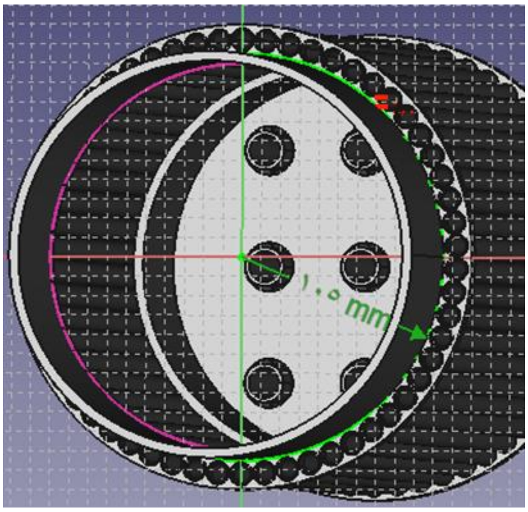
Nb of cylinder : 58

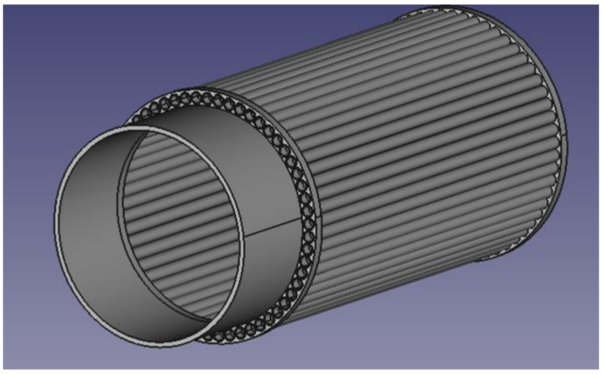
Int diameter : 10 mm

Ext diamter: 12 mm

Fuel (H2/Methan) Burner Unit



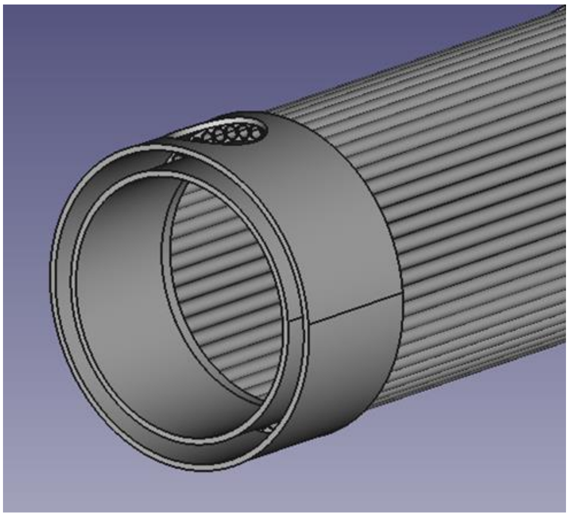




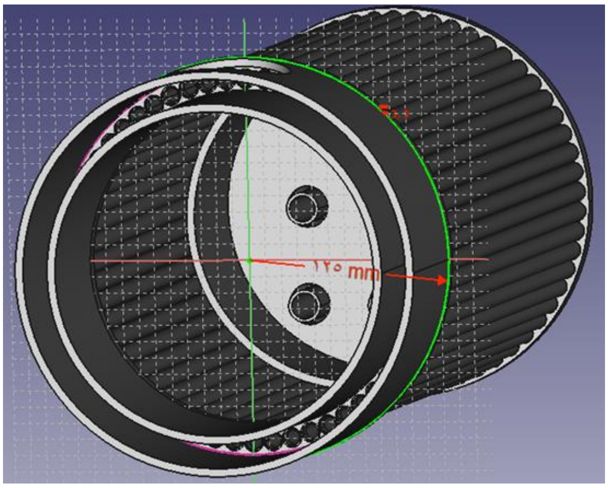
Length : 10 cm

Int diameter : 20 cm

Ext diameter : 21 cm



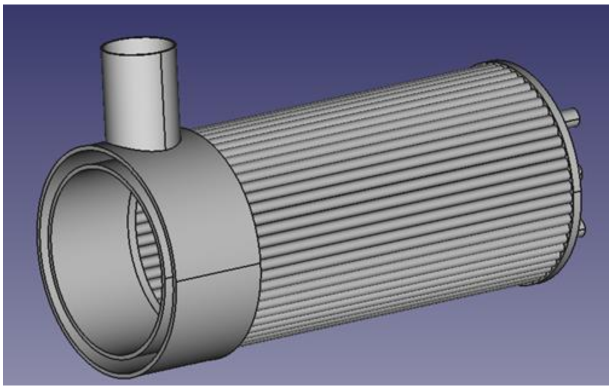
Length : 10 cm

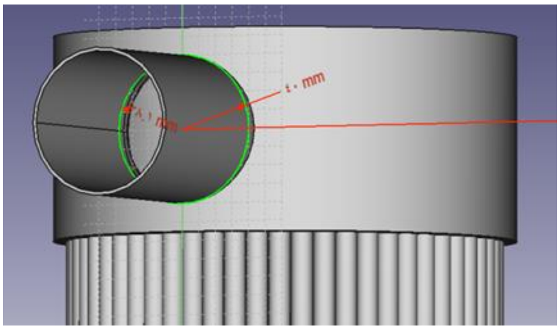


Int diameter : 24 cm

Ext diameter : 25 cm

Fuel (H2/Methan) Burner Unit

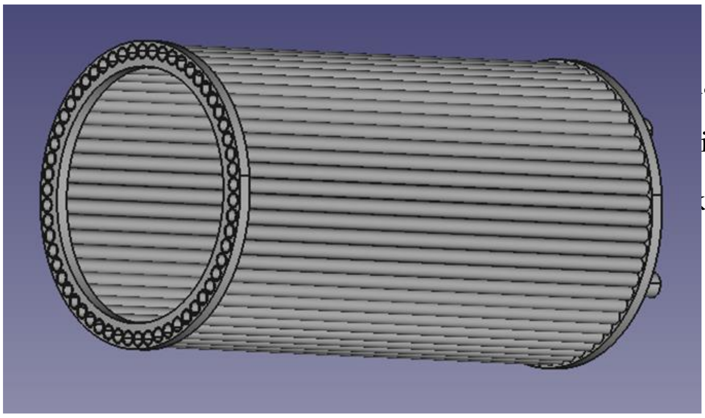




Height : 10 cm

Radius 1 : 1.5“

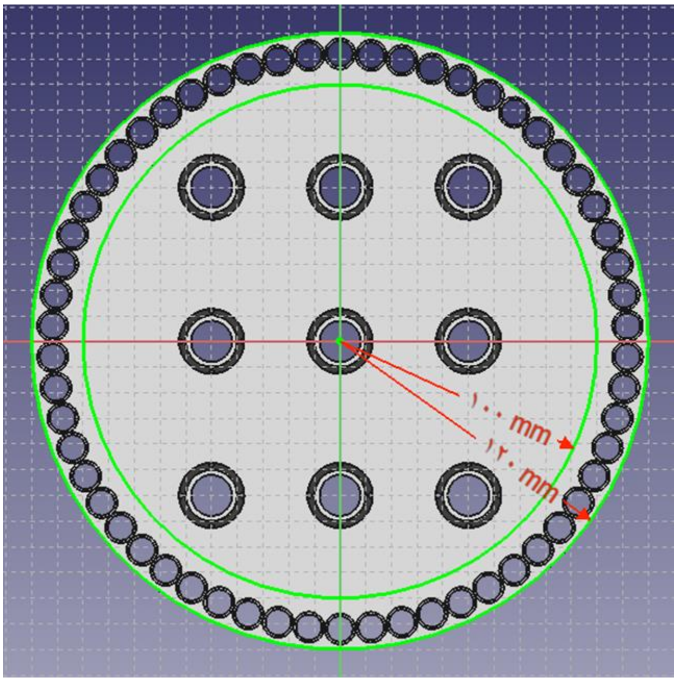
Radius 2 : 4 cm



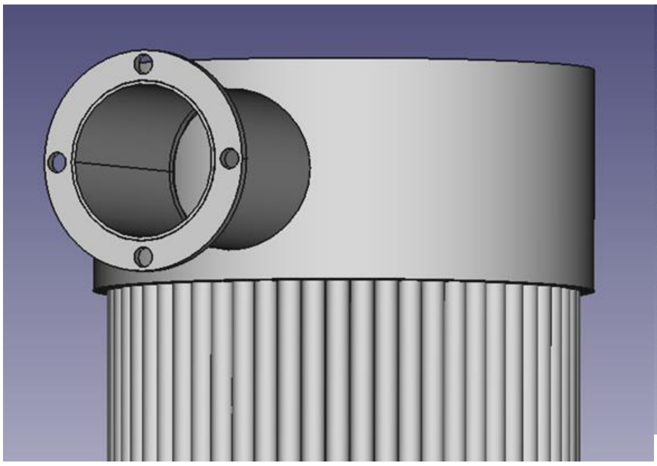
ameter : 20 cm

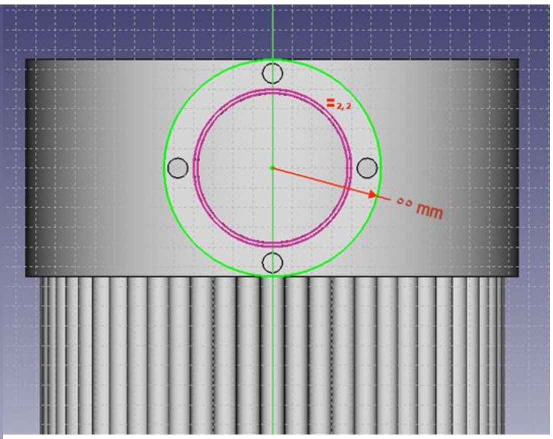
iameter : 24 cm

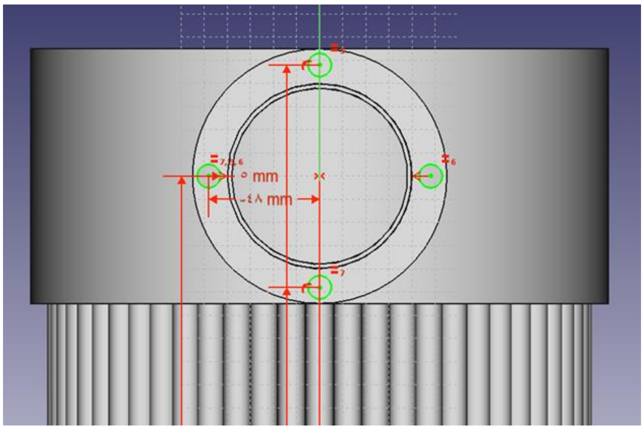
ness : 1 cm

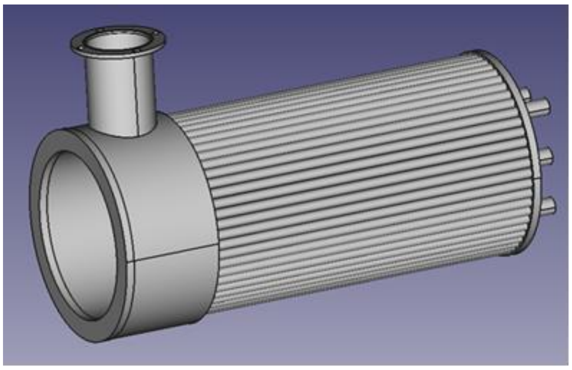


Fuel (H2/Methan) Burner Unit







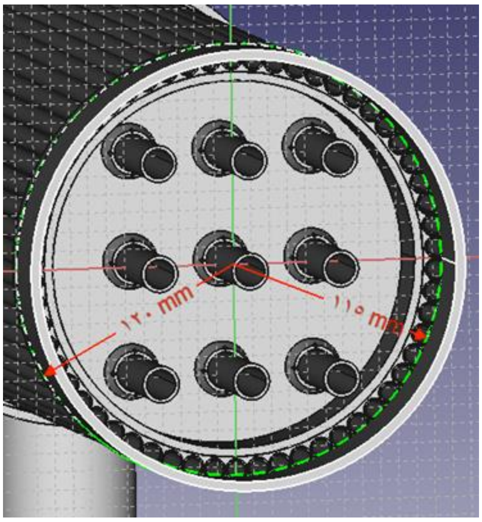


Int diameter : 20 cm

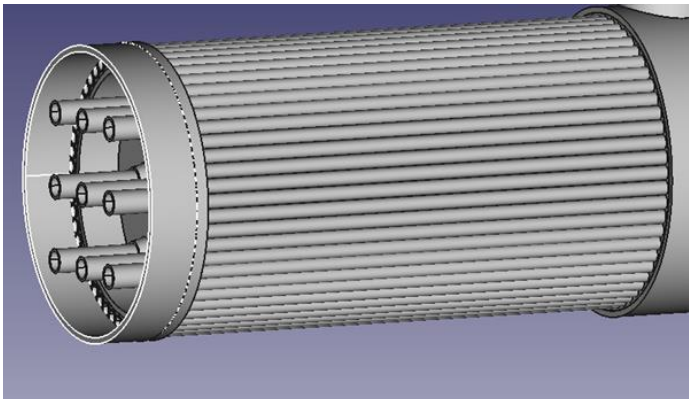
Ext diameter : 25 cm

Thickness : 1 cm

Fuel (H2/Methan) Burner Unit

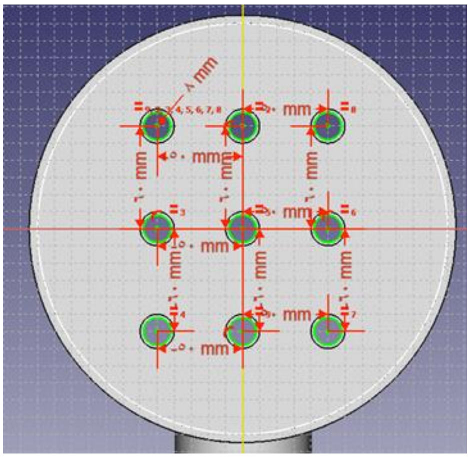


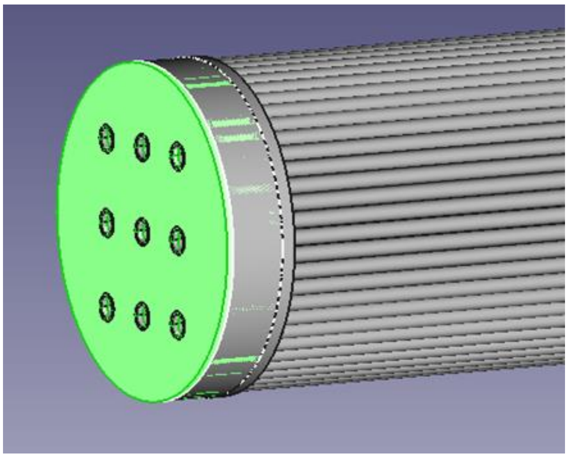
Length : 3.5 cm



Int diameter : 23 cm

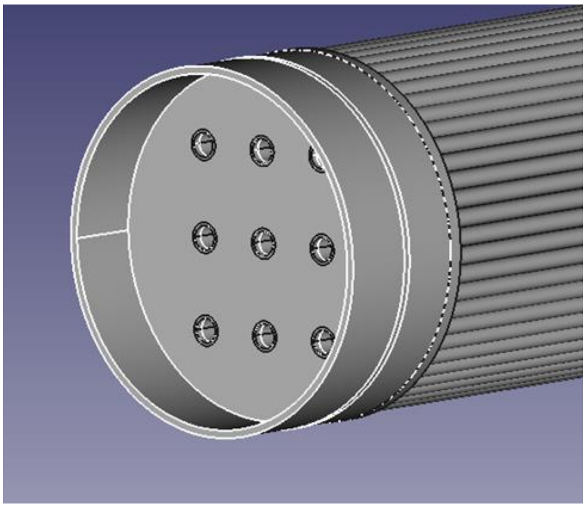
Ext diameter : 24 cm

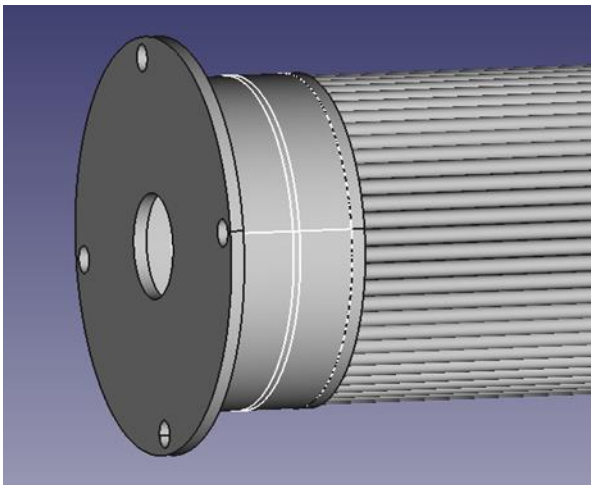




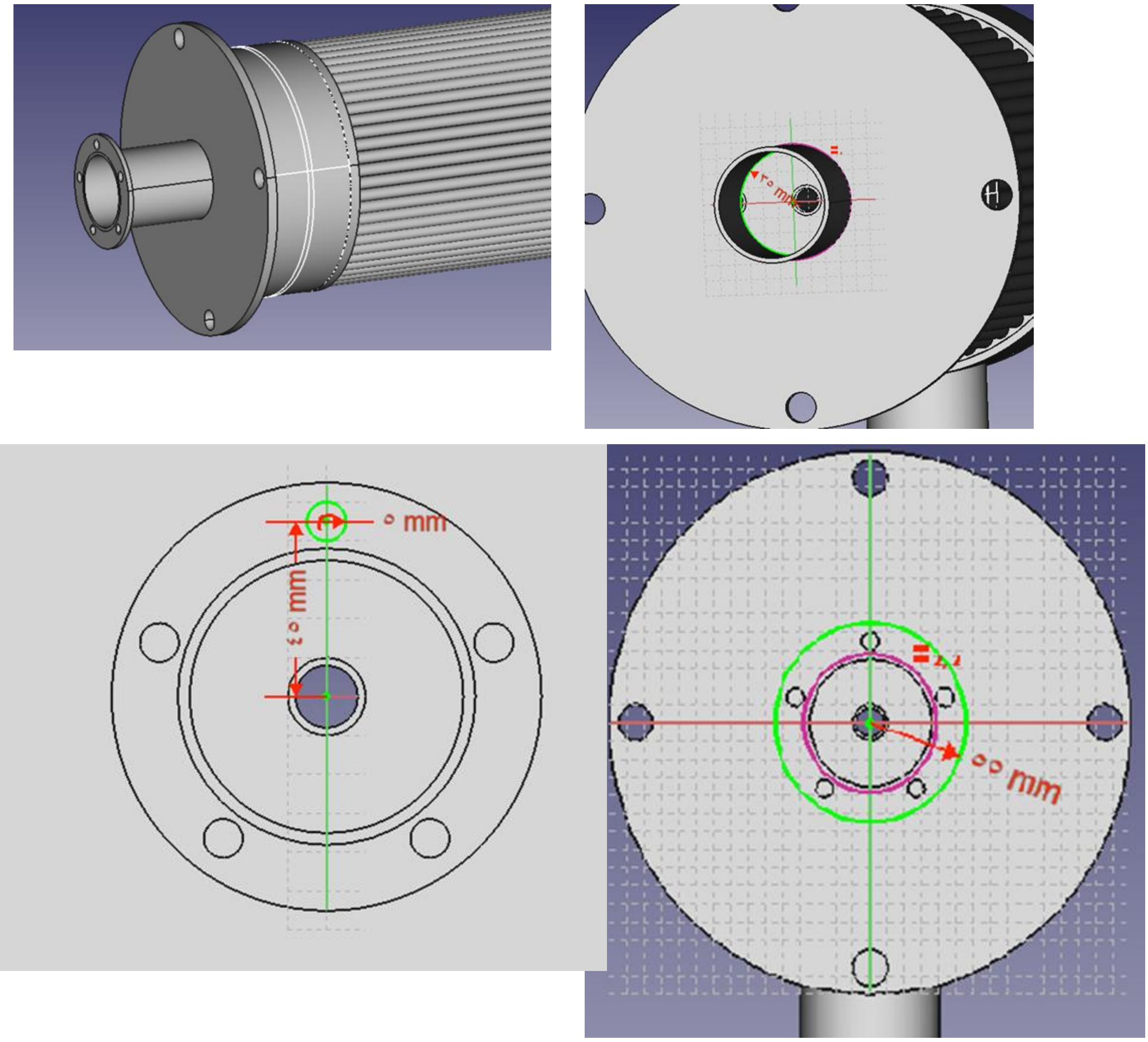
Thickness: 5mm

Length : 5 cm

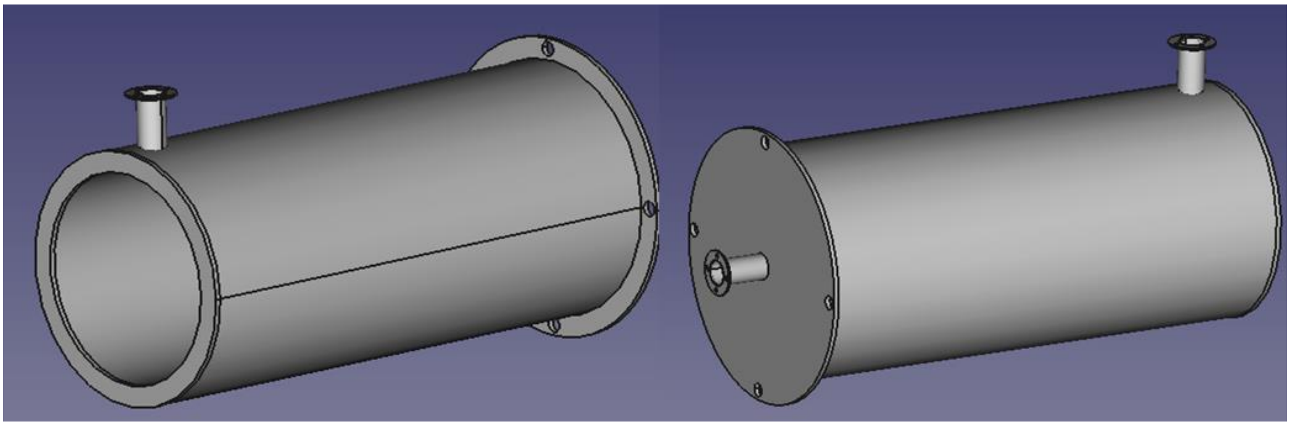


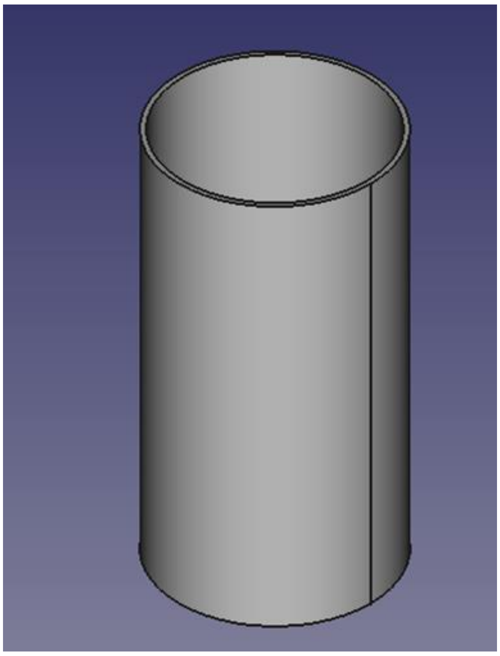


Fuel (H2/Methan) Burner Unit



Design 2

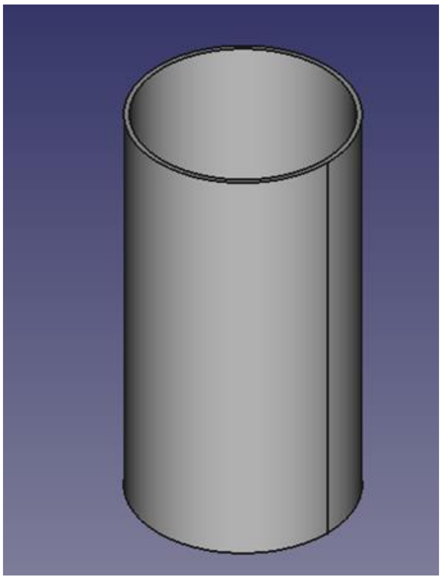




Int diameter: 23 cm

Ext diameter: 25cm

Length: 50 cm

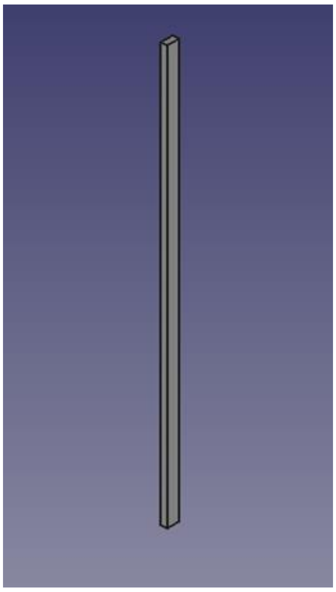


Int diameter : 17 cm

Ext diameter : 20 cm

Length : 40 cm

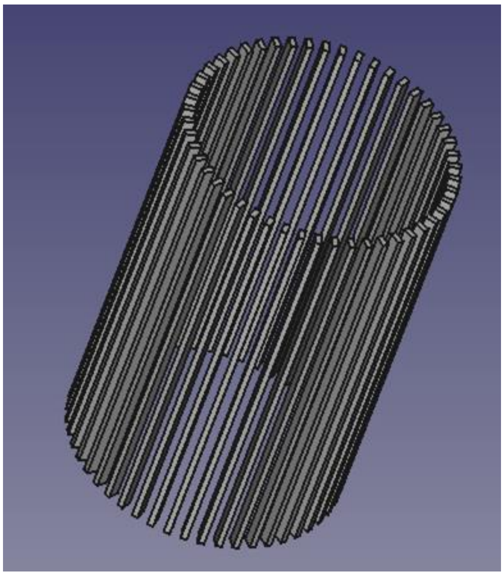
Fuel (H2/Methan) Burner Unit



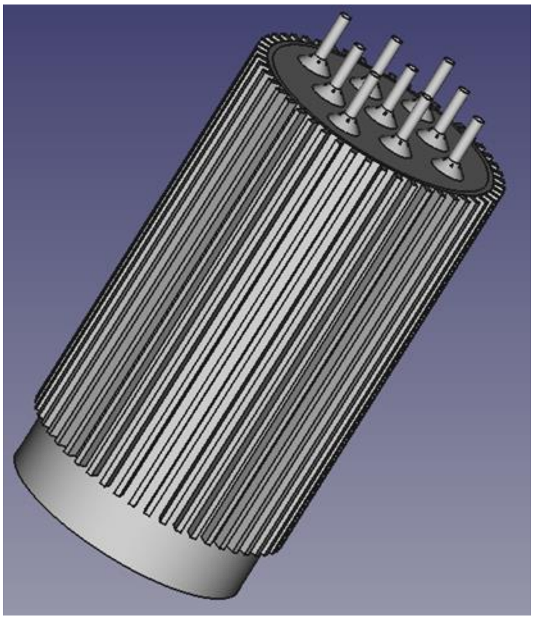
length: 1 cm

width : 5mm

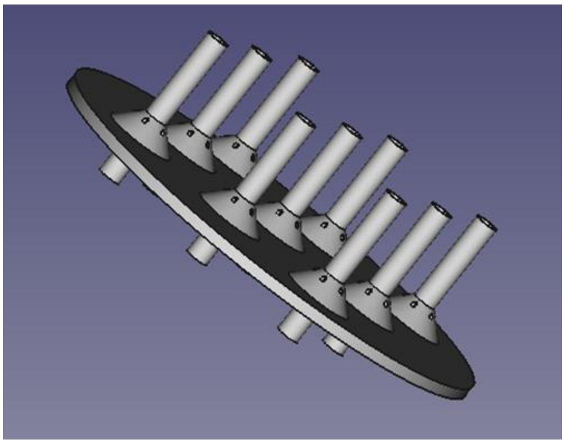
height : 35 cm

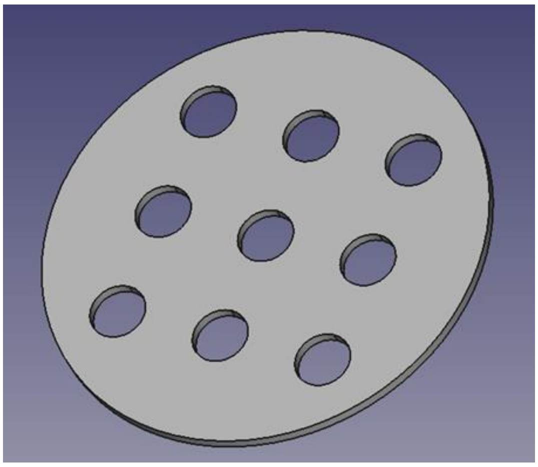


Nb of bars : 50



Fuel (H2/Methan) Burner Unit

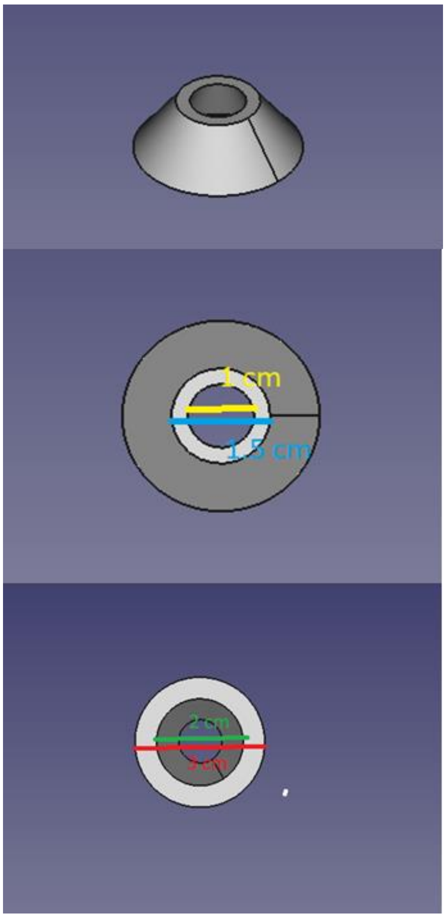




Dimetre of plate : 17 cm

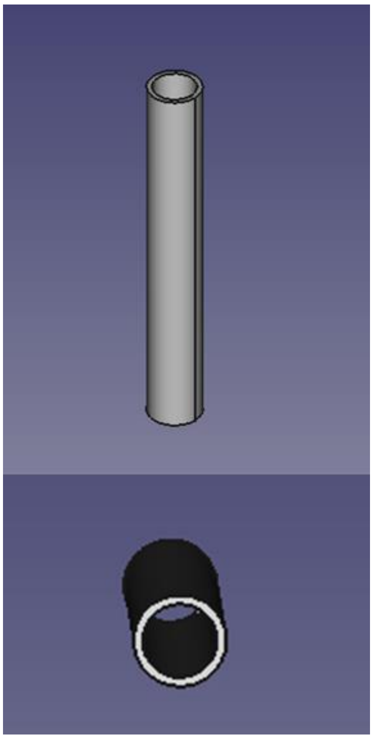
Thickness : 5mm

Diameter of holes : 25 mm



Height of cone : 1 cm

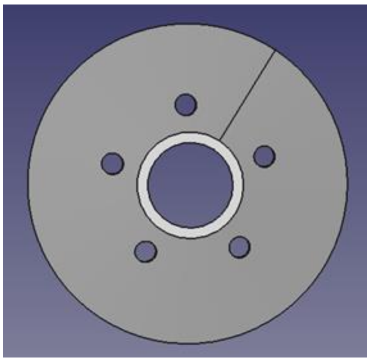
Fuel (H2/Methan) Burner Unit



Height: 7cm

Int diameter: 8 mm

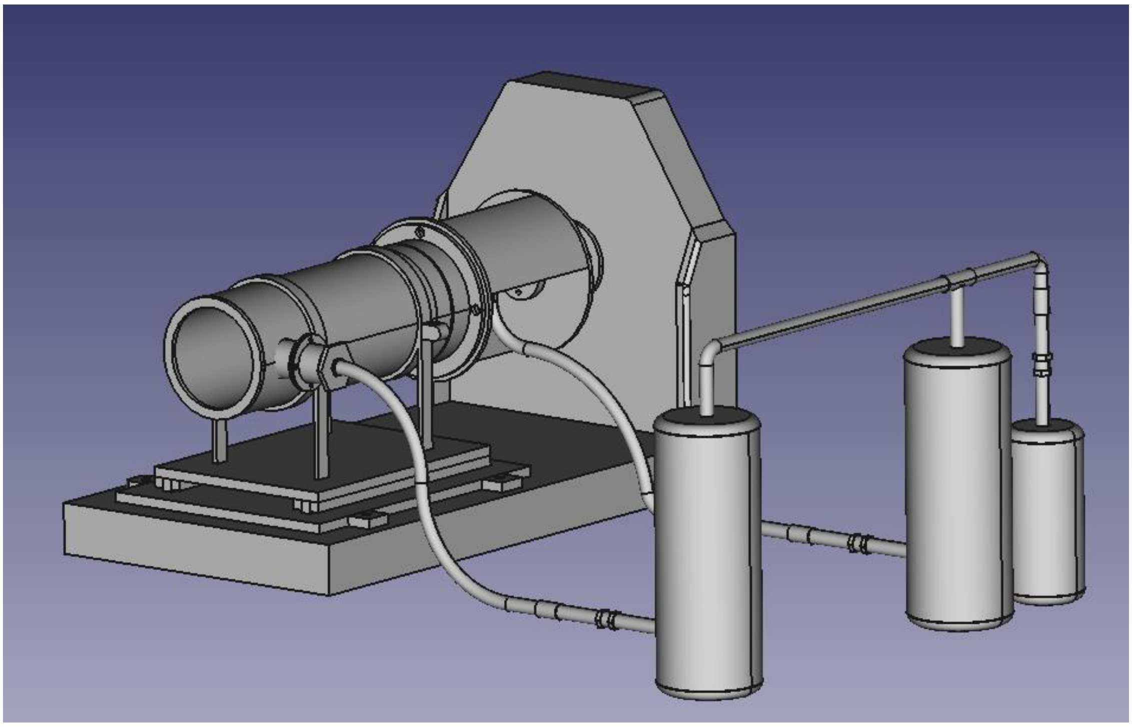
Ext diameter: 10 mm

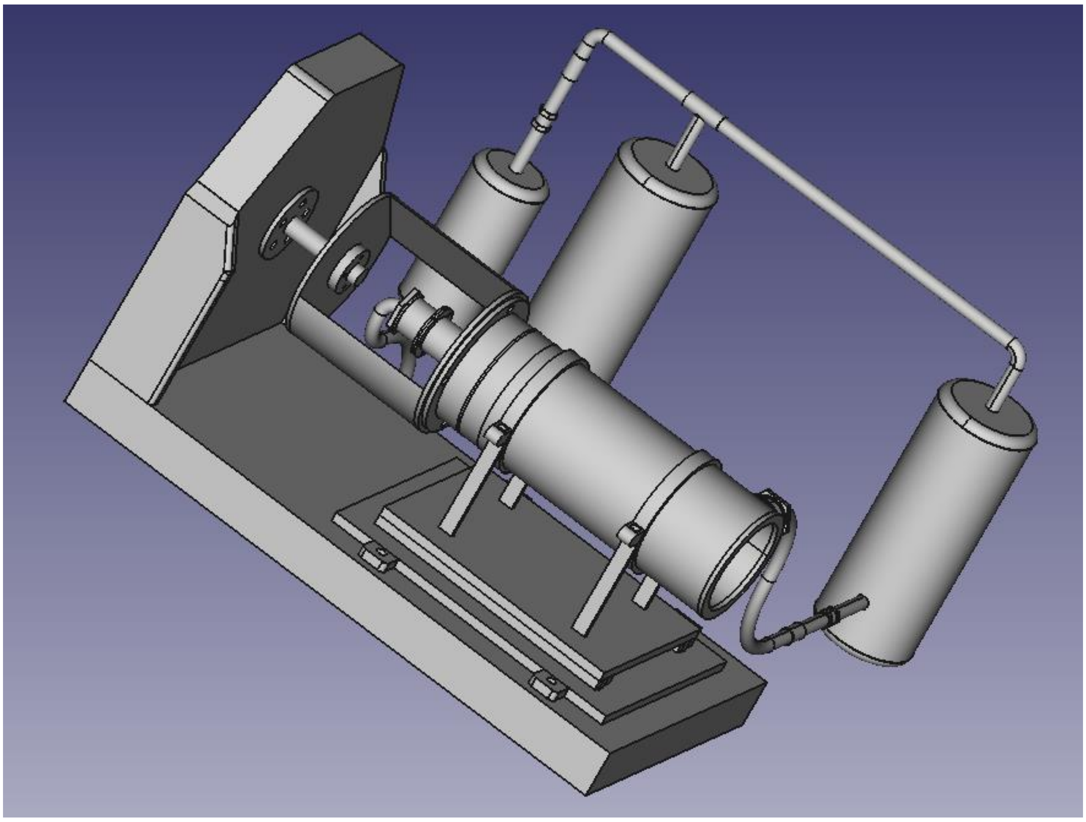


Diameter of holes : 2 mm

fule_burner_261218.FCStd

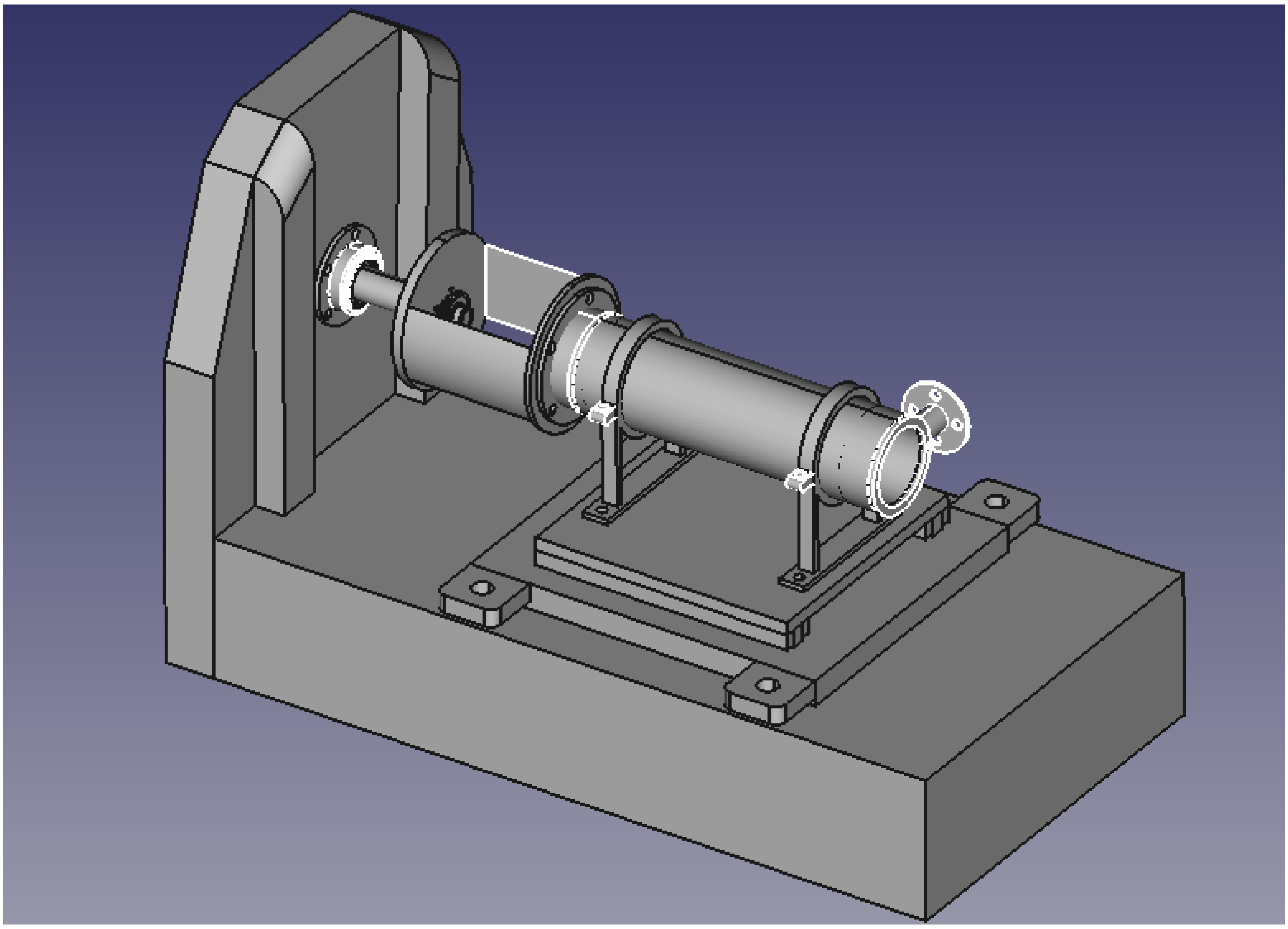
Holder & fuel burner





holder+fuleburner_05
1118.FCStd

Fuel (H2/Methan) Burner Unit



Fuel burner test rig

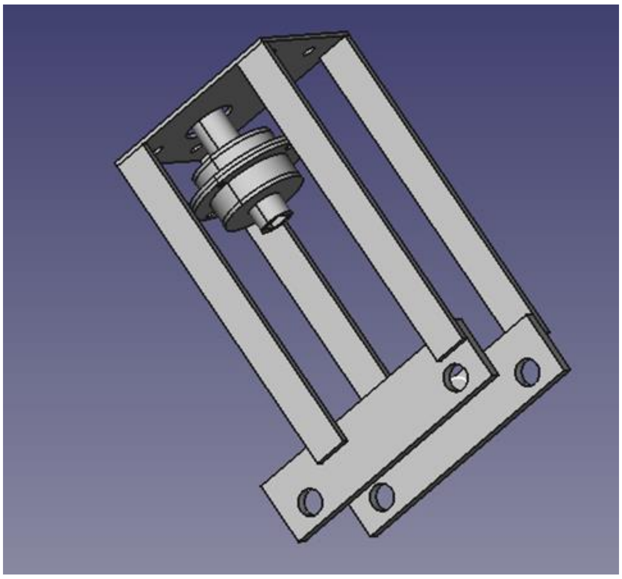
fuel_burner_04_08_18.FCStd

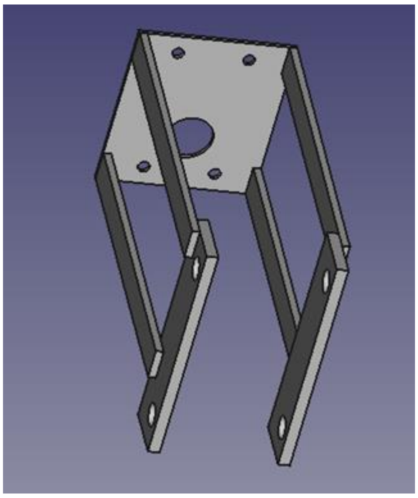
11 Electric valve motor healder

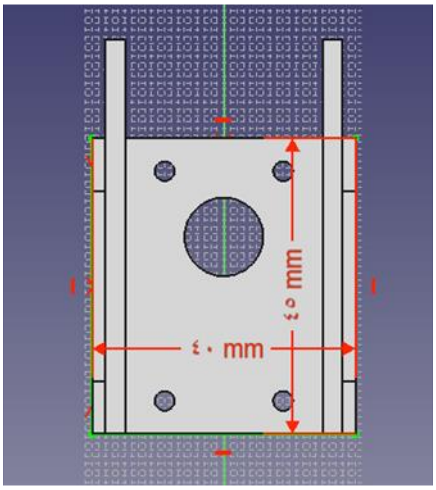
Electric valve 12V DC

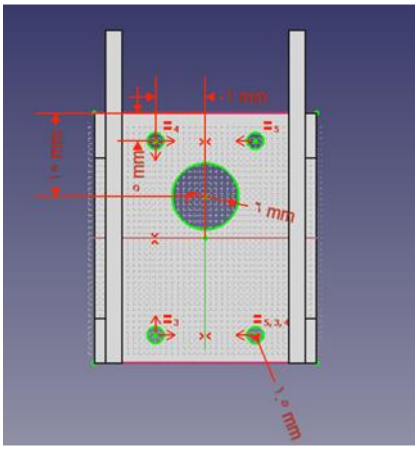
11.1 Design system

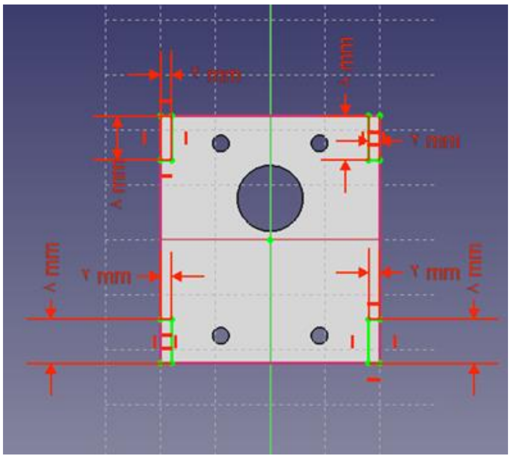
__Design 1:__

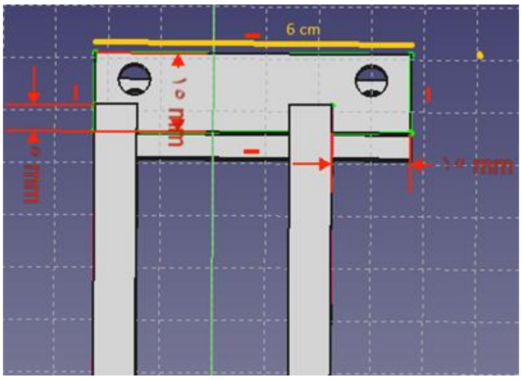




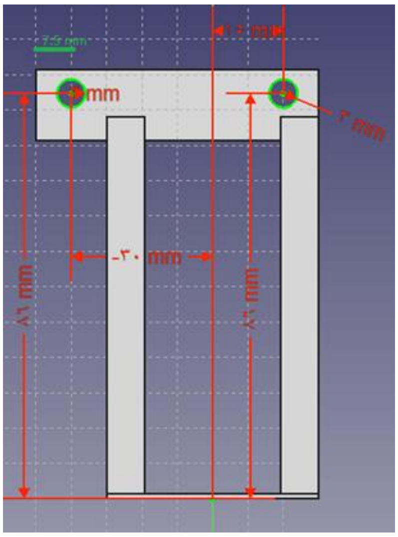


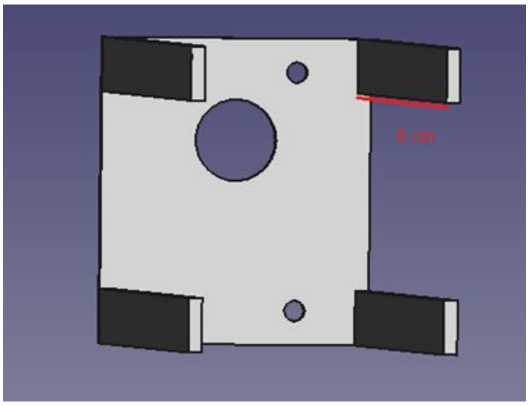


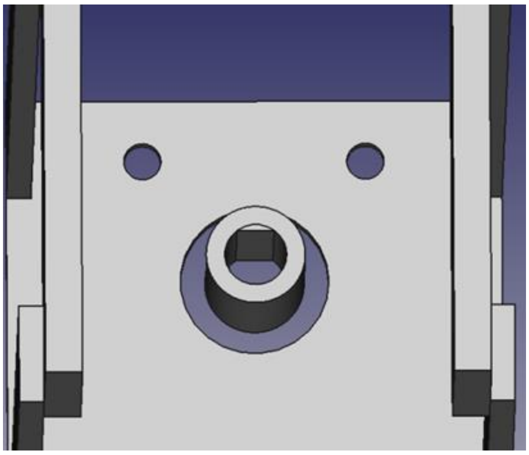


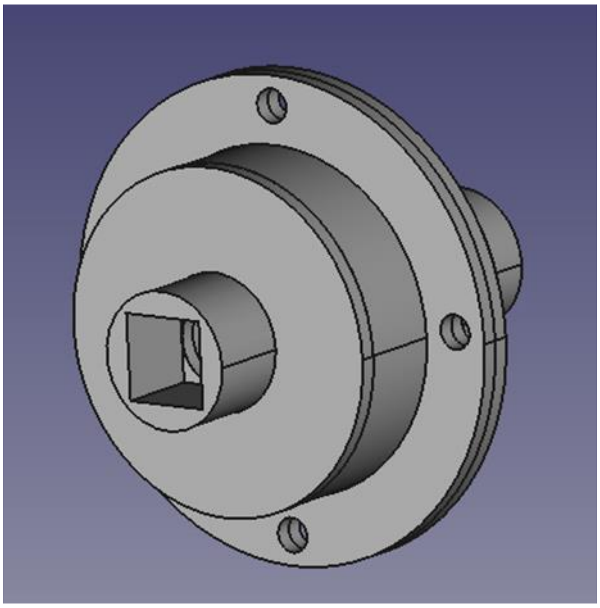


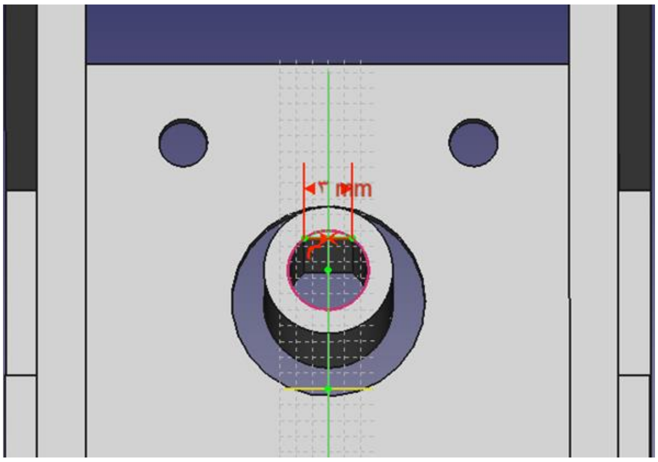
Electric valve motor healder

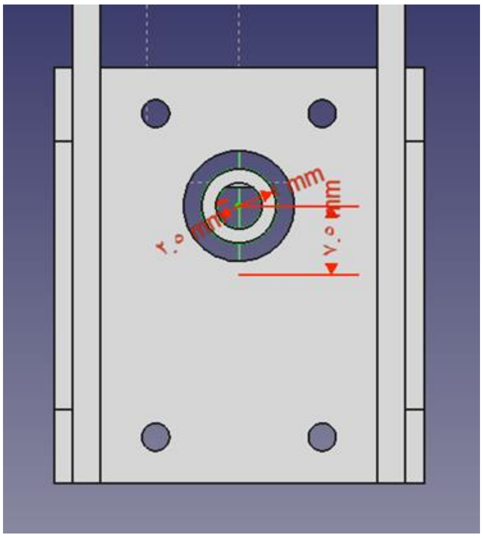




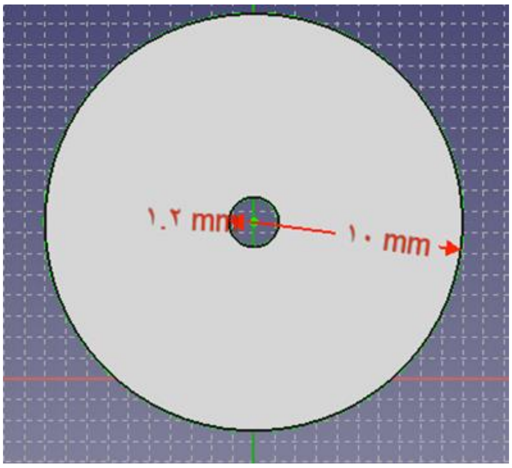


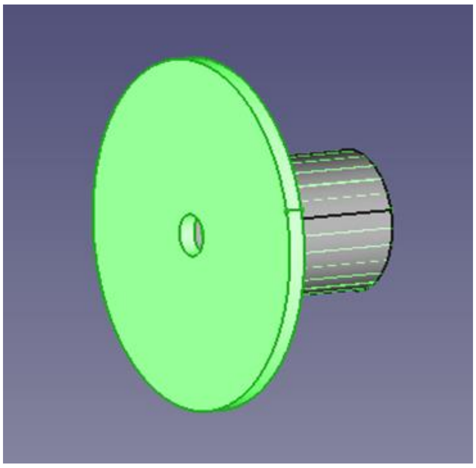


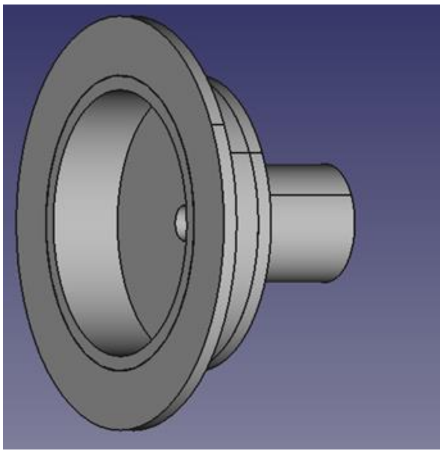


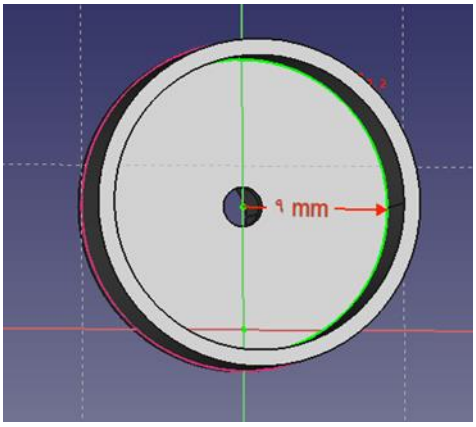


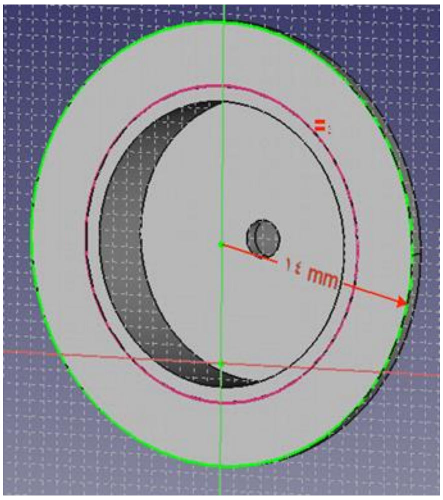
Electric valve motor healder



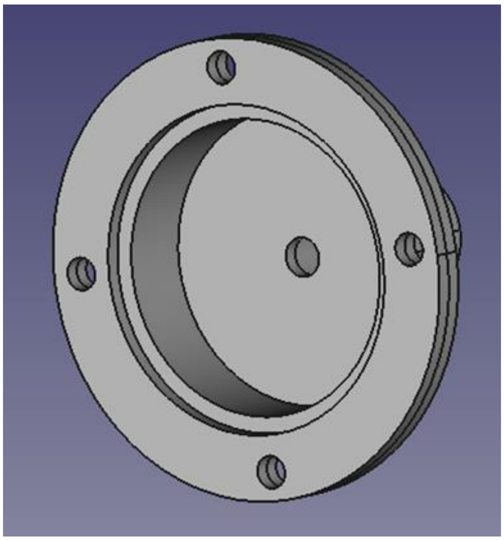


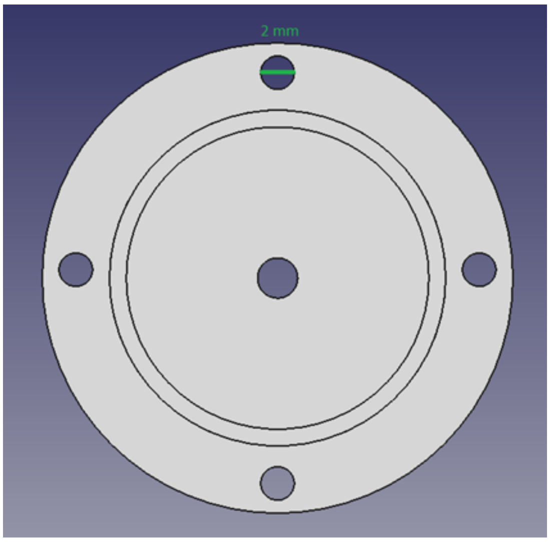


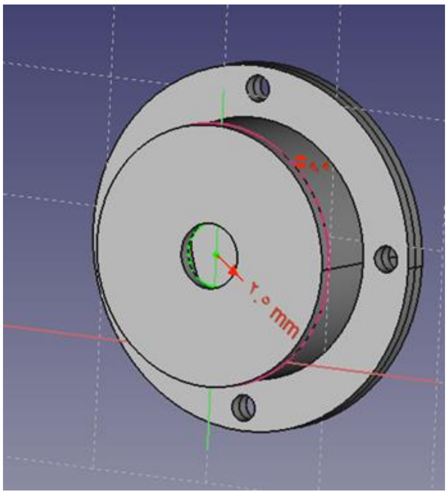


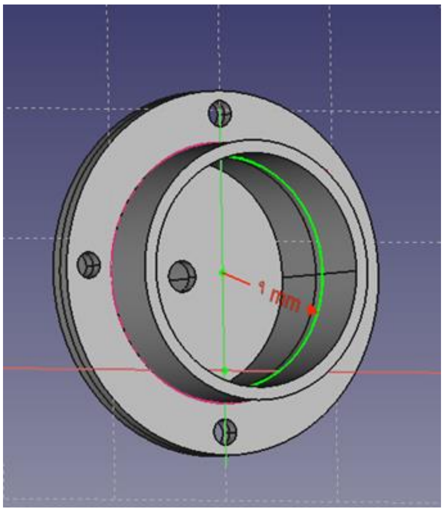


Electric valve motor healder









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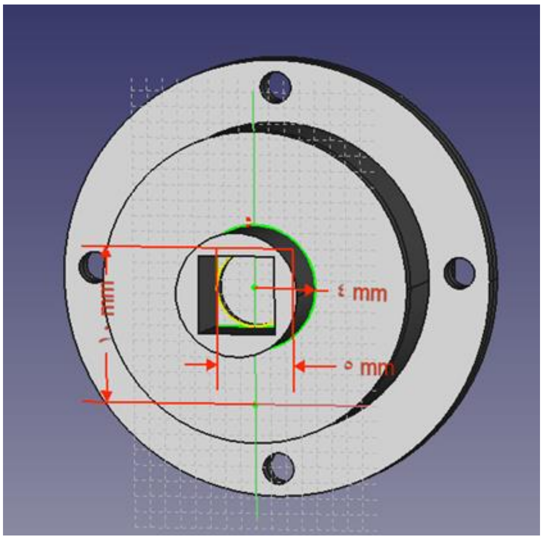
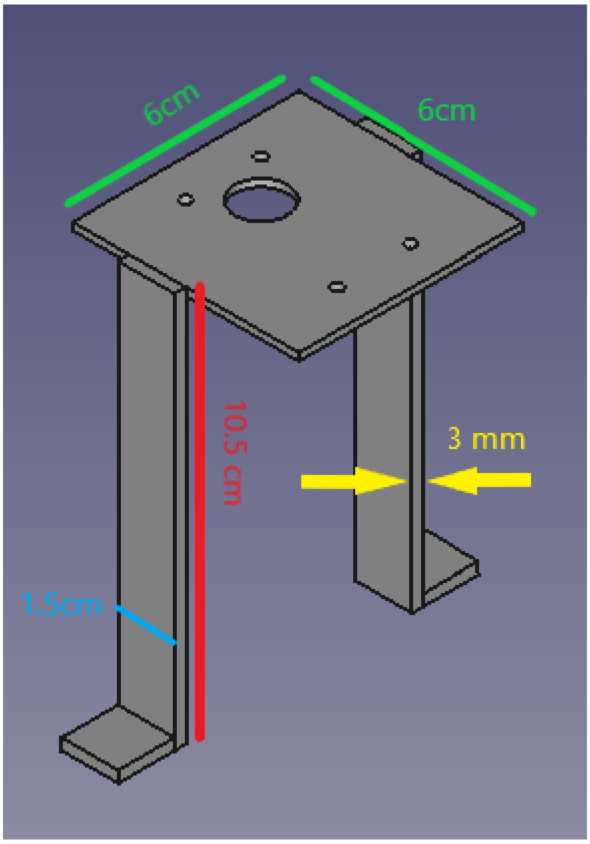
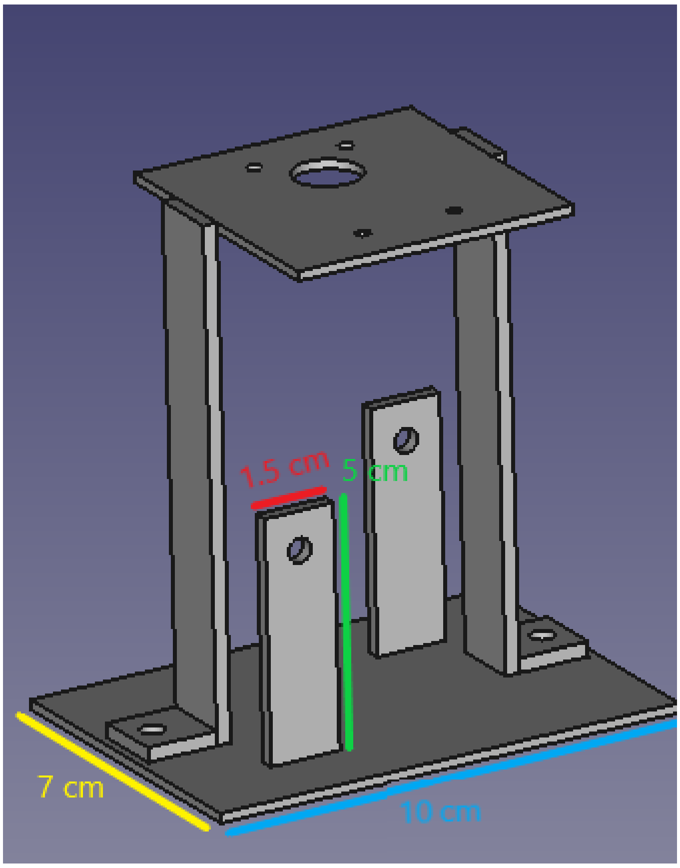
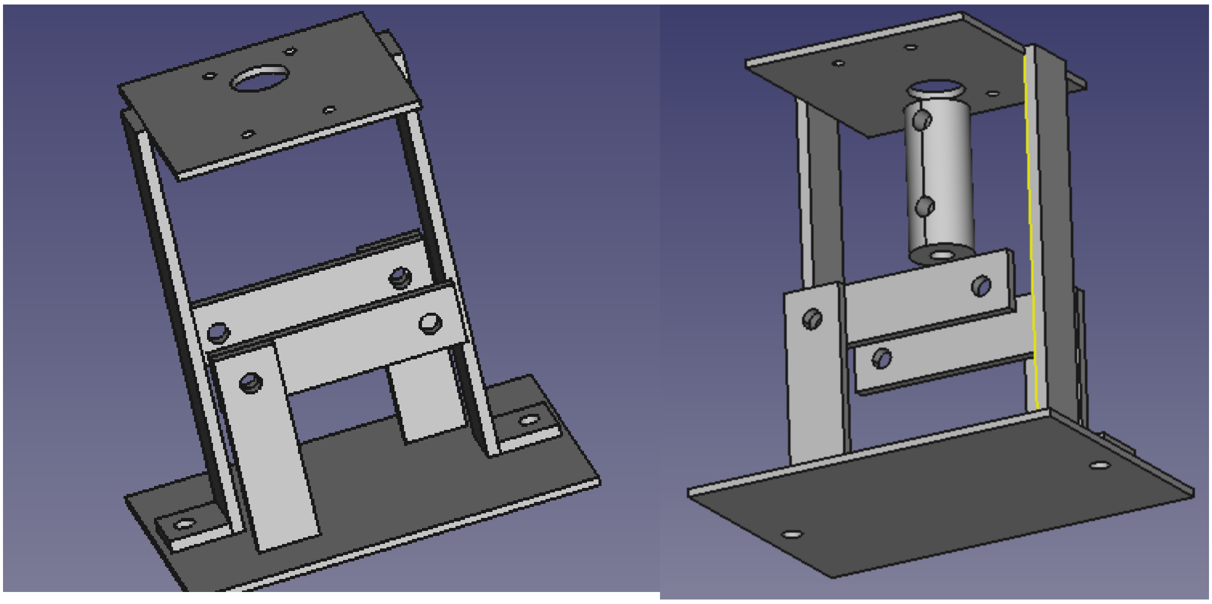


Electric valve motor healder

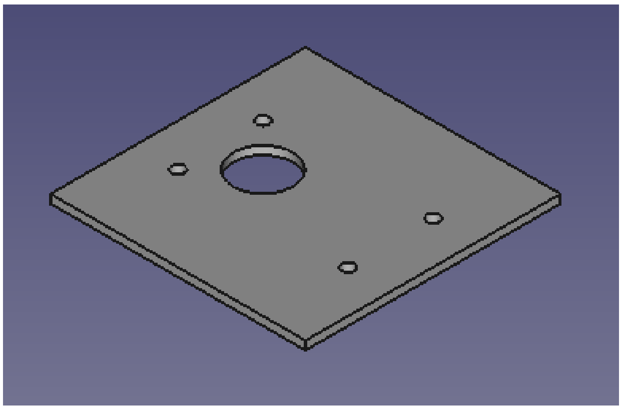
Design 2:

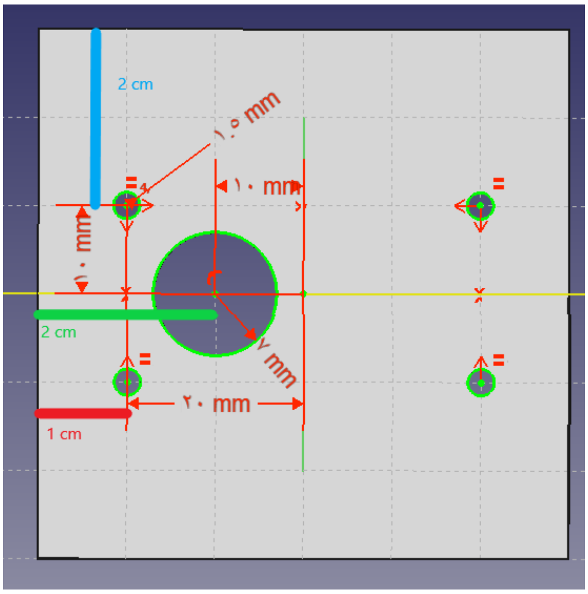


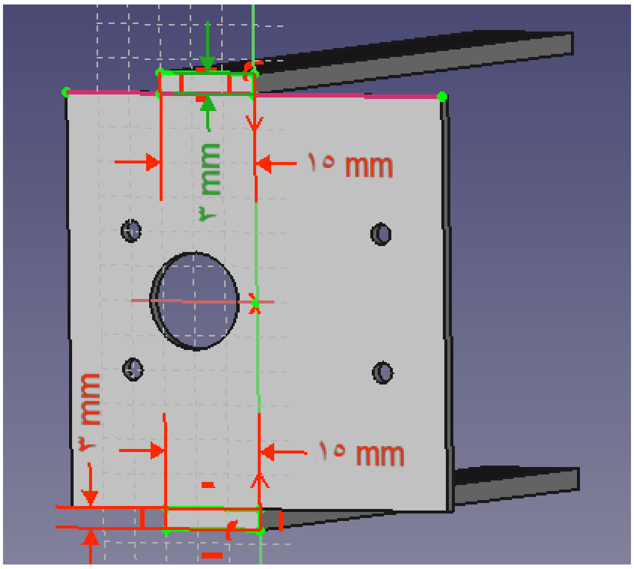


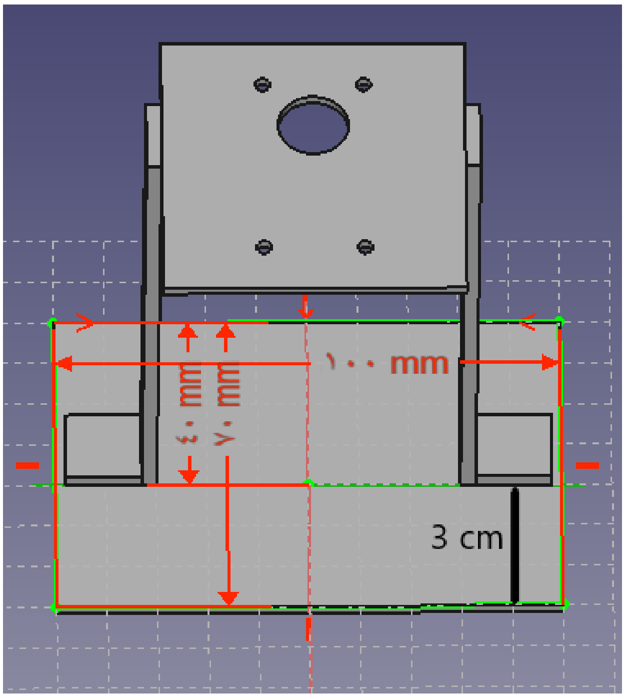


Electric valve motor healder

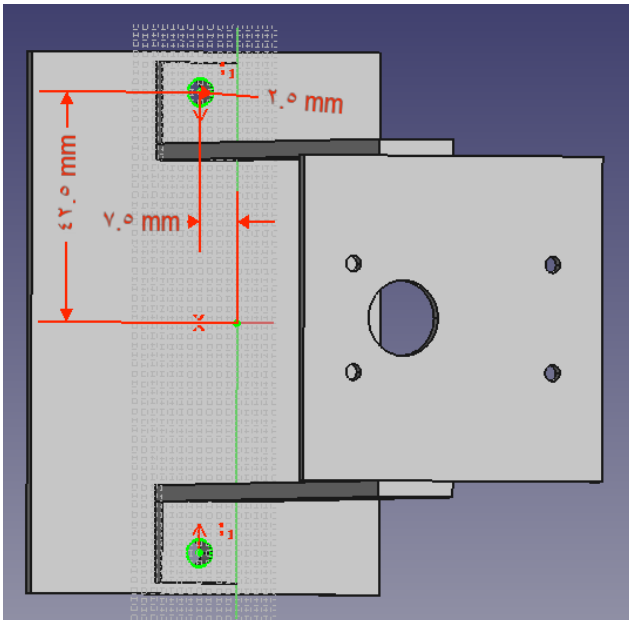


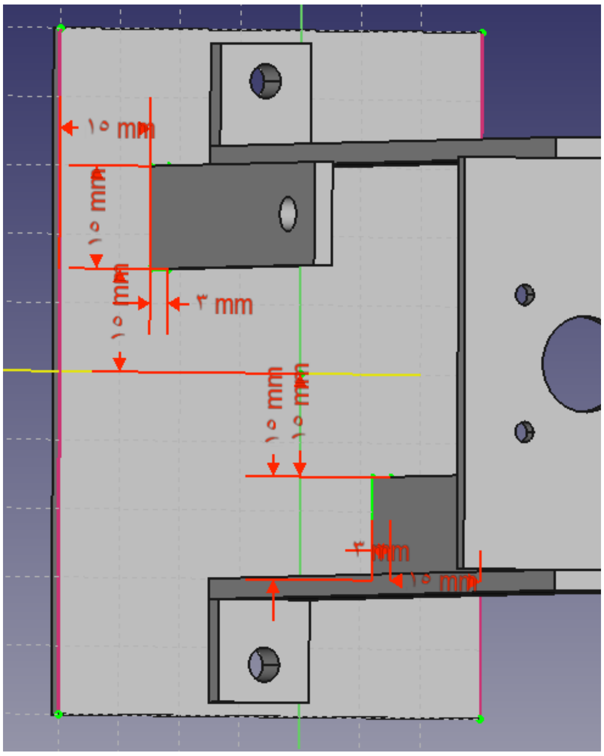


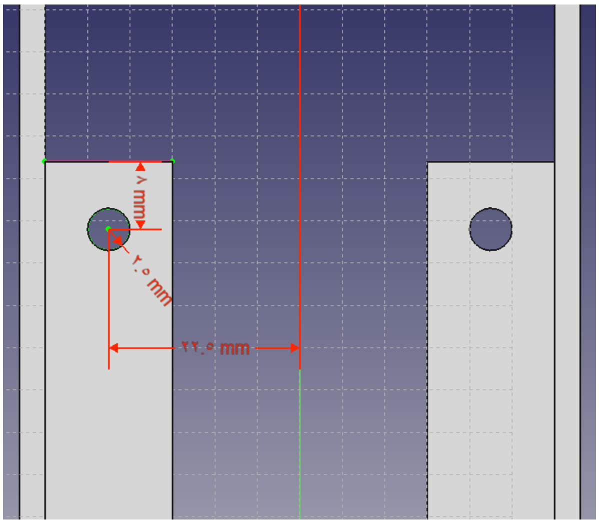


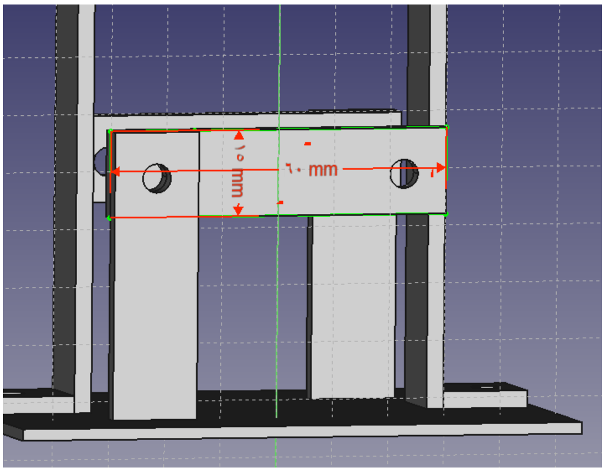


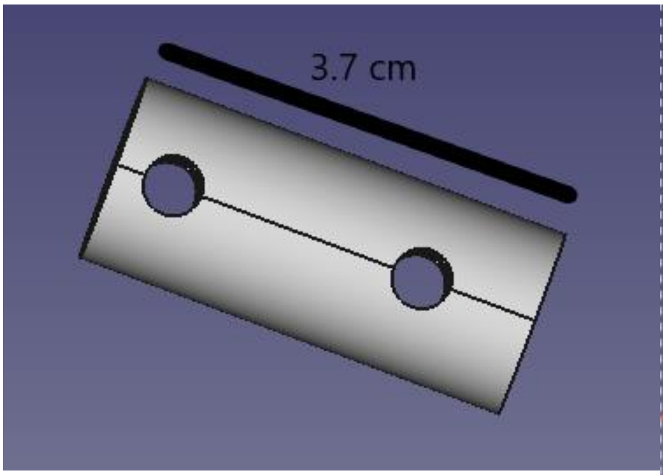
Electric valve motor healder

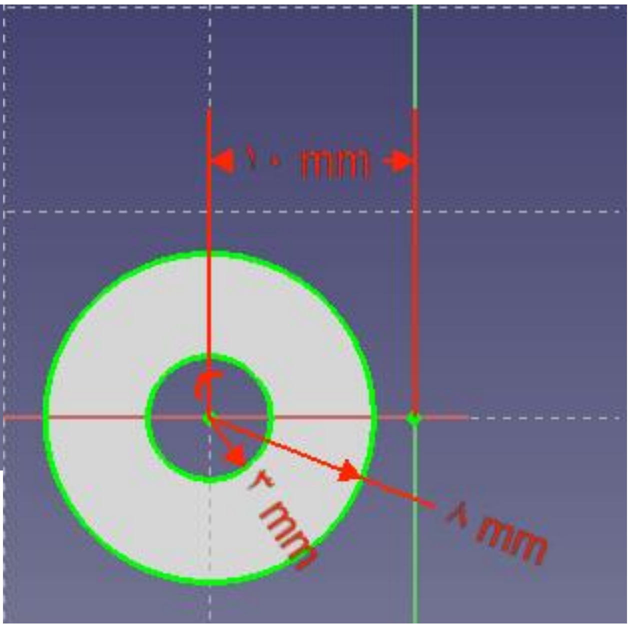




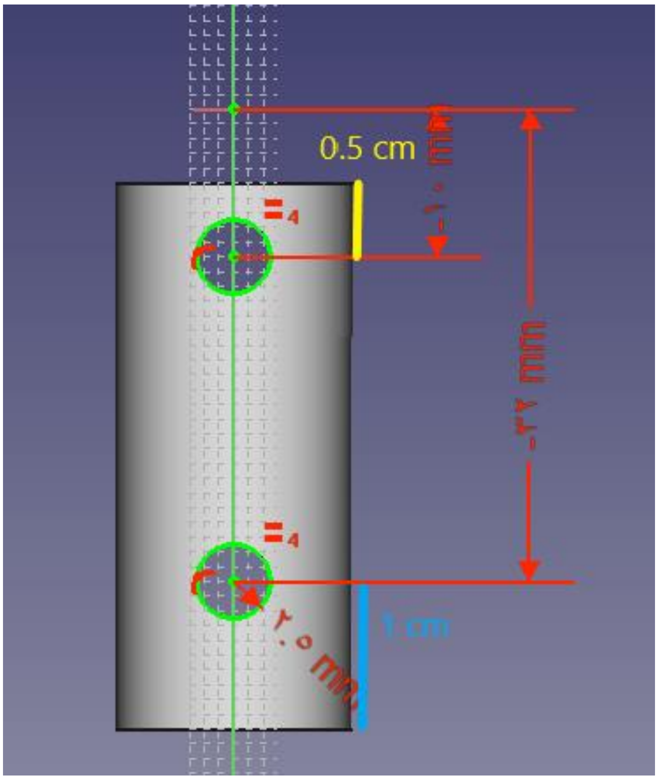








Electric valve motor healder



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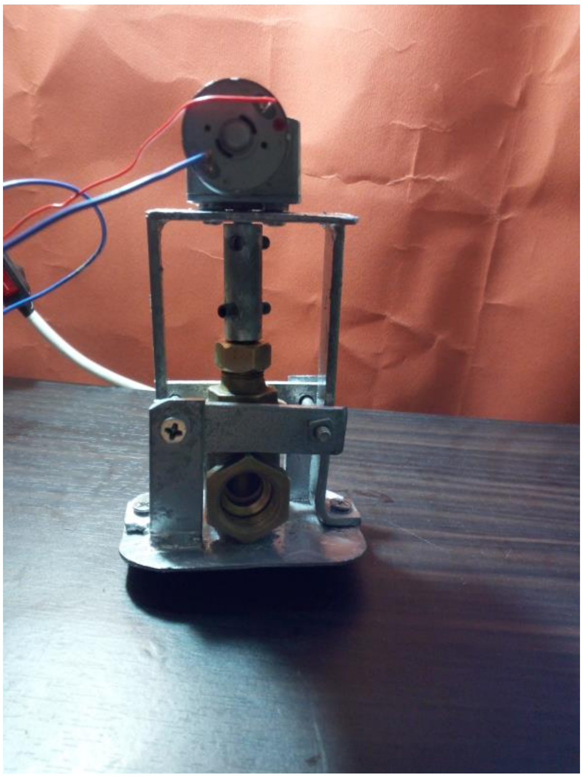
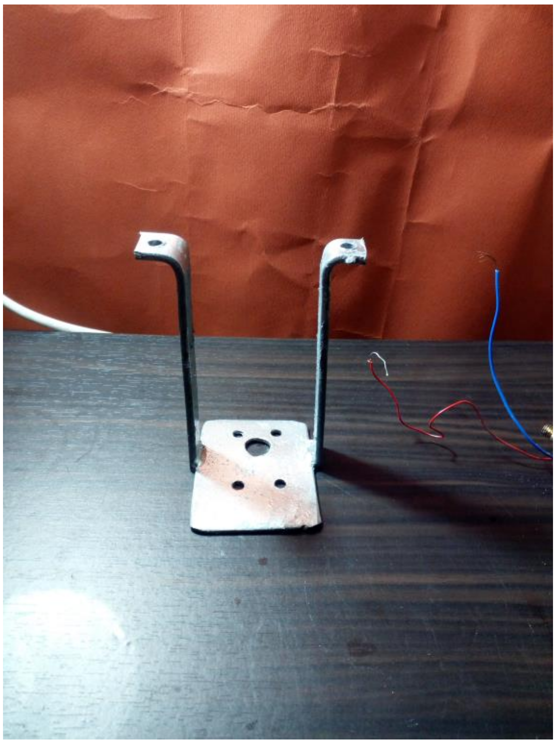
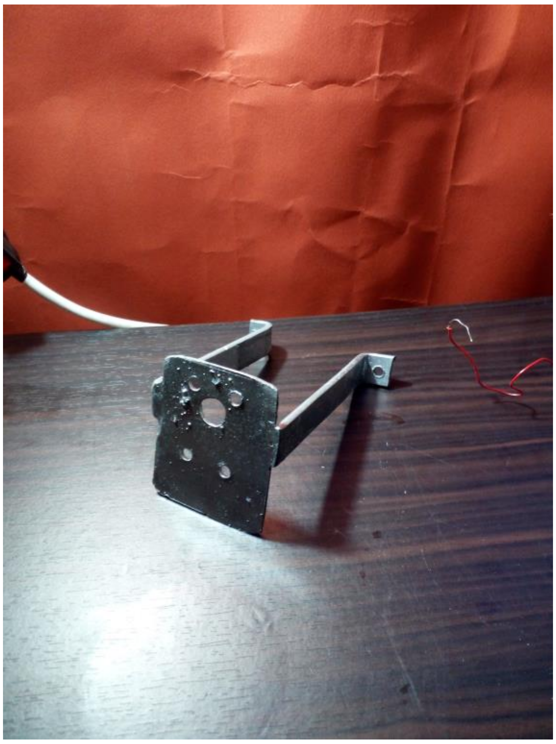
261218.FCStd

<u>Manufacturing design 2 :</u>

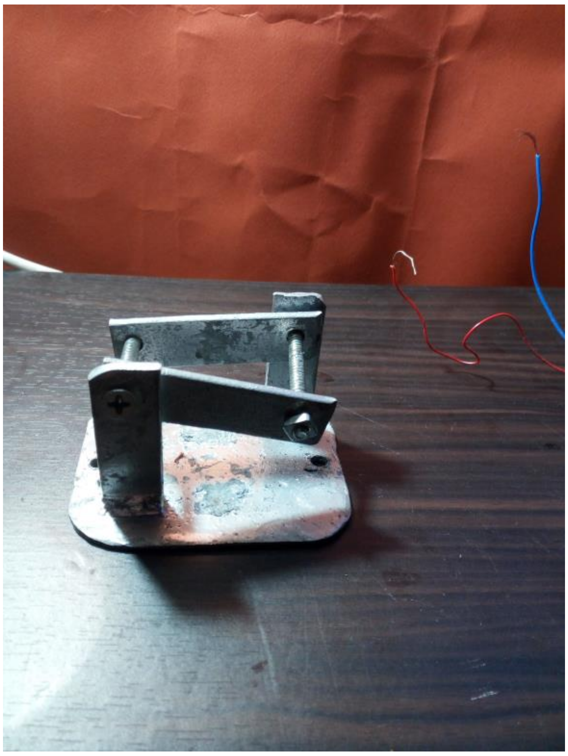
Electric valve motor healder







Electric valve motor healder

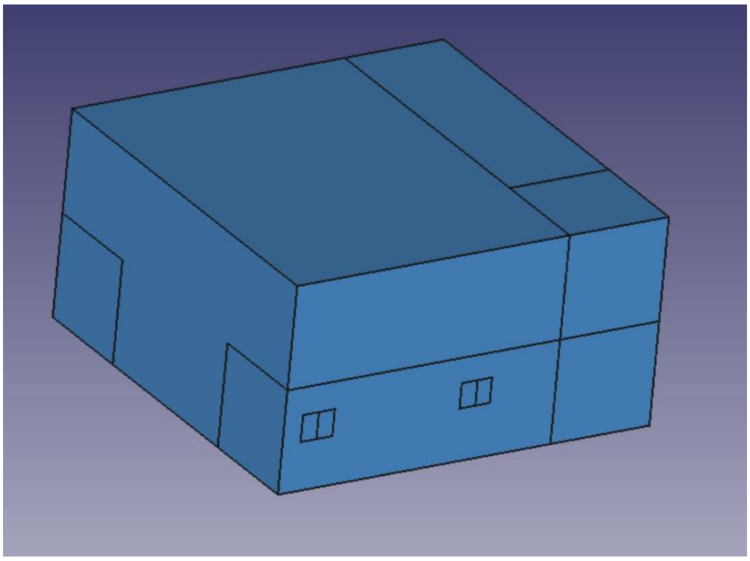


Electric valve motor healder

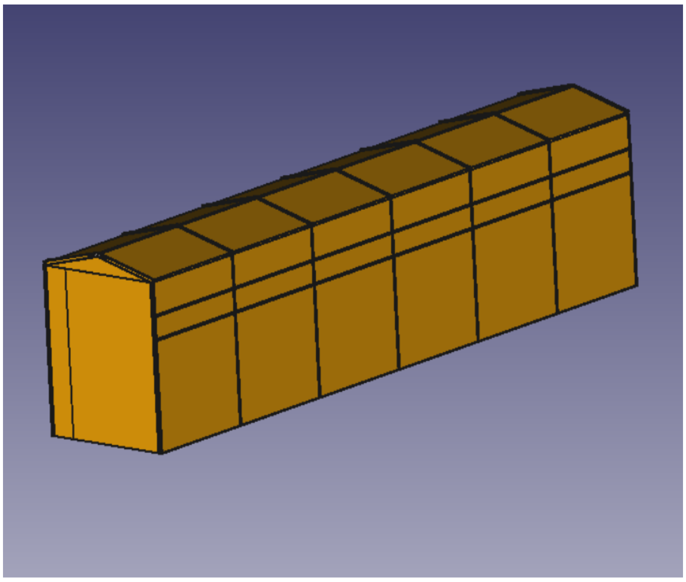
Electric valve motor healder

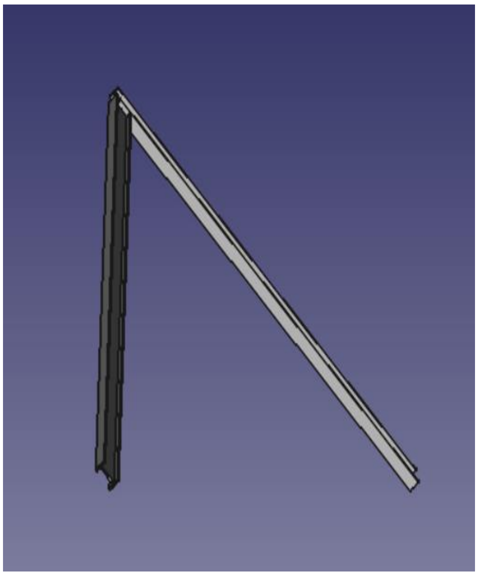
4 electric valve

12 المكتب (office)



13 هنغار (Production Hangar)

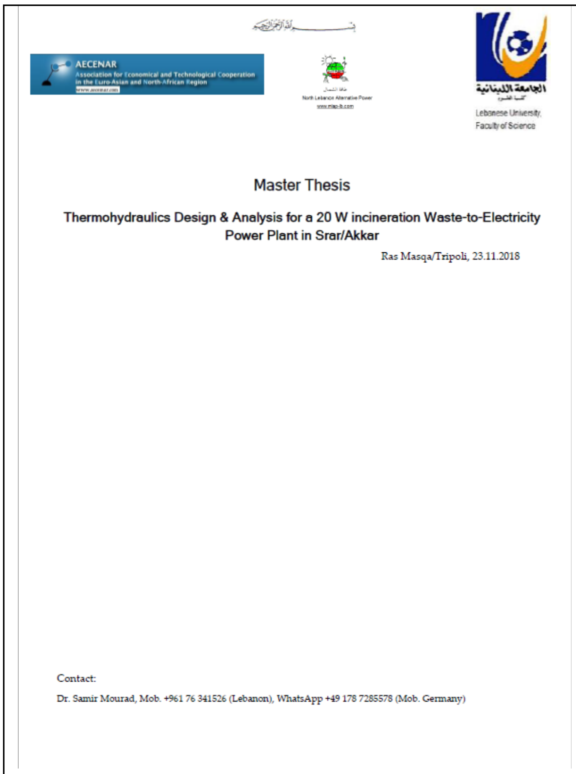




Length:24 m

Height : 5 m

14 Master Thesis Tasks for 2019



بسم الله الرحمن الرحيم

AECENAR
Association for Economical and Technological Cooperation in the Euro-Asian and North-African Region
www.aecenar.com

طاقة الشمال
North Lebanon Alternative Power
www.nlap-lb.com

الجامعة اللبنانية
كلية العلوم
Lebanese University,
Faculty of Science

Master Thesis

Thermohydraulics Design & Analysis for a 20 W incineration Waste-to-Electricity Power Plant in Srar/Akkar

Ras Masqa/Tripoli, 23.11.2018

Contact:

Dr. Samir Mourad, Mob. +961 76 341526 (Lebanon), WhatsApp +49 178 7285578 (Mob. Germany)

بسم الله الرحمن الرحيم

AECENAR
Association for Economical and Technological Cooperation in the Euro-Asian and North-African Region

MEAE – A member of AECENAR Applied Research Center
www.aecenar.com/institutes/meae

طاقة الشمال
North Lebanon Alternative Power
www.nlap-lb.com

الجامعة اللبنانية
كلية العلوم

Discipline
Energetic physics

Master Thesis proposal

Laboratory name: AECENAR
Laboratory website: http://www.aecenar.com

Supervisors (contact persons)
Samir Mourad, smourad69@googlemail.com, Mob. +961 76 341 526

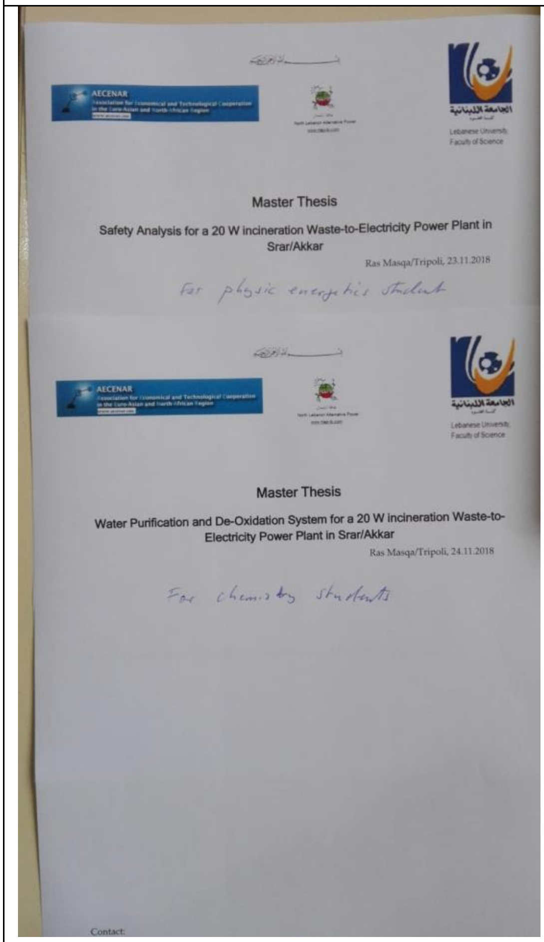
Ras Masqa/Tripoli, 21.02.2018

Thesis title: Design, Regulation and Test of gas turbine for a biogas power plant

Working packages:

- Reading and searching about the subject (2 Weeks) (http://www.aecenar.com/publications)
- Detailed design for the cylinder, rotor, and blades (3 Weeks)
- Waste incineration based regulation concept for the turbine (e.g. air supply regulation) (3 weeks)
- Support of the CNC machine based manufactoring of the turbine (4 weeks) (- 15 June 16)
- Test of the delivered turbine with the NLAP (2 weeks) (- 30 June 16)
- Calculation of the efficiency of the turbine (1 Week)
- Documentation (4 Weeks).

Key Words: alternative energy, FreeCAD / AutoCAD, gas turbine regulation, cylinders, rotor, blades, CAM (Computer Aided Manufacturing)



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North Lebanon Alternative Power

الجامعة اللبنانية
Lebanese University,
Faculty of Science

Master Thesis

Safety Analysis for a 20 W incineration Waste-to-Electricity Power Plant in Srar/Akkar

Ras Masqa/Tripoli, 23.11.2018

For physic energetics student

بسم الله الرحمن الرحيم

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North Lebanon Alternative Power

الجامعة اللبنانية
Lebanese University,
Faculty of Science

Master Thesis

Water Purification and De-Oxidation System for a 20 W incineration Waste-to-Electricity Power Plant in Srar/Akkar

Ras Masqa/Tripoli, 24.11.2018

For chemistry students

Contact:

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