Amine Based Carbon Capture Technology

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APPROVAL SHEET

This dissertation submitted by **Ms. Sana Rasool, Ms. Seemal Mushtaq, Mr Syed Aon Bukhari** and **Ms. Fatima tu Zahra Zaman** is accepted in its present form, by the Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Islamabad as satisfying the requirement for the degree of Bachelors in Environmental Engineering.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

ABSTRACT

Fuel is being burnt at an ever increasing rate to meet human requirements. Approximately 55 % of global warming is believed to have been caused by CO_2 emissions. Little variations in temperature may cause drastic changes in global environment and geography. The problems of Global warming and climate change are now spiraling out of control, triggering catastrophic events worldwide.

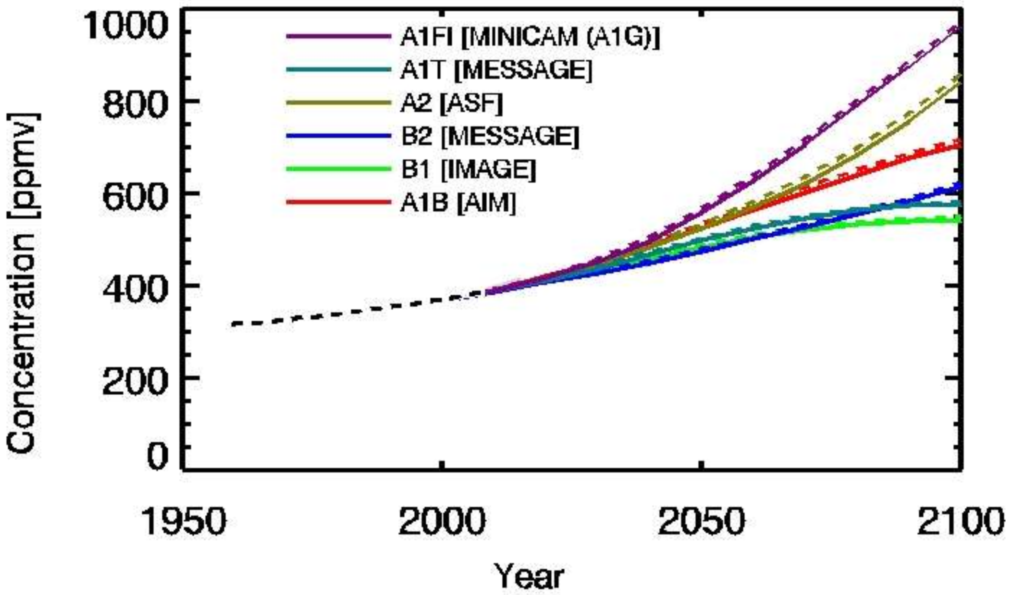
Even though Pakistan contributes less than 0.5 % of total GHG, it suffers severe effects of global warming and climate change effects. From floods, heat waves to record breaking cold spells, Pakistan is experiencing the consequences of imbalance in earth's ecosystem. This calls for global measures for CO_2 capture and sequestration. This research discusses the background of amine based CO_2 capture technology and conducts a laboratory scale research to test its compatibility in industries. A lab scale CO_2 scrubber prototype has been designed and fabricated, with CO_2 removal efficiency of 96%. This study also compares efficiency using 30 % and 20 % by weight of both MEA and DEA as amine solvent. It draws conclusions to discuss the viability of CCS with amines at industrial level in Pakistan.

1. INTRODUCTION

Industrial revolution has resulted in significantly higher levels of Carbon dioxide (CO_2). A direct consequence of this increased CO_2 concentration is the rise in global mean temperatures. Although, the co-relation between higher CO_2 levels in the atmosphere and rising temperatures is still debatable among some scientists, the association cannot be overlooked or dismissed. Over the past few decades, global warming and climate change have emerged as two of the most significant issues of the 21st century. Natural calamities such as floods, Glacier Lake Outburst Floods (GLOFs), climate extremes i.e. heat waves and cold spells have disturbed the delicate, intricate radiation balance of the earth and resulted in loss of life and resources worldwide.

Carbon is introduced into the atmosphere everyday by a variety of sources including fossil fuel emissions, deforestation, industrial emissions, transportation etc. The ocean and forests act as sinks for this CO_2 generated due to natural and anthropogenic activities (Charney, 1979). The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4) stated that ‘‘approximately 50% of a CO_2 increase will be captured naturally from the atmosphere within 30 years and an additional 30% will take another few centuries’’ (Denman *et al*., 2007). It is however, a point of concern to note that the 50% CO_2 resource discussed in the IPCC report is merely for smaller emissions and does not necessarily hold true for future large-scale industrial emissions. In addition, the carbon sinks available to the natural ecosystems may soon be highly saturated rendering them less effective if not completely non-functional, to capture and absorb CO_2 (Eby, 2009). This decline of earth’s natural sinks itself is an alarming situation as it results in direct land and ocean pollution. Deforestation is causing habitat destruction at a massive scale and over the recent decades, we have seen what is perhaps, the fastest biodiversity decline rate in recorded history. In addition to climate change CO_2, increase also has an impact on the chemistry of world’s oceans. Ocean water becomes more acidic due to the increase in concentration of CO_2 levels. Calcium carbonate that is the main shell or skeleton of many aquatic organisms starts to dissolve due to the acidic nature of the water of the ocean. This acidification phenomenon takes tens of thousands of years to revert to normal, which implies that it may be considered irreversible. If anthropogenic activities continue to produce CO_2 at the current production rates, ocean pH is estimated to fall as much as 0.5 units by 2100 (Raven, 2005). This is three times the present concentration of hydrogen ions. The scale may vary from region to region however; this is an alarming figure and will result in catastrophic destruction of marine life. **Figure 1.1** shows the concentration of CO_2 in the atmosphere. In such circumstances, CO_2 sequestration seems to be the only option available to environmental experts.

Figure 1.1: Concentration of CO_2 in the Atmosphere[1],[2]



The increase in CO_2 can be accounted as following

- More than 6.5 billion people burn fuel to keep warm, to provide electricity to light their homes and to run industry, and to move about using cars, buses, boats, trains, and airplanes.

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[1] Intergovernmental Panel on Climate Change (IPCC), Carbon Dioxide: Projected emissions and concentrations, 20 June 2013, http://www.ipcc-data.org/observ/ddc_CO2.html, Accessed on **17 December 2013**

[2] CO_2 concentrations derived from EPICA and Vostok ice cores. The red bar at the side indicates the evolution of the Mauna Loa measurements. On this time scale, the 50 years of measurements span less than the thickness of the line, so it appears vertical.

- The burning of fuel releases CO_2 to the atmosphere.
- Six Giga-tons of carbon is added to the atmosphere due to burning of fossil fuels each year.
- CO_2 concentrations in the atmosphere have risen from about 270 ppm million (0.026%) to about 380 ppm (0.038%) after the initiation of industrial era.
- CO_2 is a greenhouse gas, and the increased concentration of carbon dioxide in the atmosphere must influence earth's radiation balance.

Anthropogenic activities worldwide release tons of CO_2 into the atmosphere, land and oceans every year. This CO_2 is causing temperature and radiation imbalances, reduction and suppression of certain crop growth, climate extremes such as heat wave in Russia in 2005 and cold spells, loss of biodiversity, food and water crisis in the developing world due to loss of livelihood, flooding due to glacier melting and much more. We have only just begun to realize the magnitude of the problem and by the time we are able to control the CO_2 we have already released until now, there would be a lot more to handle.

It is this very reason that calls for immediate CO_2 sequestration measures worldwide. The global community must realize that global warming and climate change are not regional problems but global ones that require communities to sit together and find solutions to the problem. While it is impossible and unacceptable to justify halt of industrialization processes due to their sensitive environmental outcomes, the environment at the same time, must not be compromised. Scientists and policy makers agree that if the problem is not addressed on priority basis, it may be out of our hands very soon and result in a rapid deterioration of the climatic balance. The developing world, while not being the major contributor of GHGs and other environmental pollutants, suffers the consequences of this global degradation. This calls for the first world to take responsibility to develop adaptation and mitigation strategies and address the problem.

In Pakistan, CO_2 emissions are not the major problem but its geographical location on the world map makes her a victim of climatic atrocities. In the immediate neighborhood of Pakistan, lie the Asian economic giants India and China while Russia contributes its share of emissions to the regional environment too. Siachin, the world’s highest battleground and the longest glacier in the world at 1.7 km suffers a heavy brunt of climate change (Cheema *et al*., 2010). Pakistan is a water scarce country. This makes the importance of Siachin along with Baltoro, Biafo, Askole and other local glaciers very important to Pakistan. The recent monsoon flood in 2010 took thousands of lives, destroyed livelihood and property. It was rated by the UN as the worst flood recorded in the history of humankind. The flood highlighted the importance of climate change and its consequences. It is ironic to note that while the country is perhaps among some of the cleanest in the world as far as GHG emissions are concerned, it is facing huge problems of environmental degradation. Siachin and the glaciers in the northern areas of Pakistan have been a source of interest and curiosity of the international scientist community over the last decade.

Over the years, climate change and environmental control has taken precedence in this developing country. Realization has been born and awareness has been created that unless the problem of CO_2 induced climate change is not catered for, the country could face severe catastrophes in the coming years. Heavy military activity, especially on the Indian side is melting the Siachin glacier and causing flooding. The region has been seismically active in the last few years, which demands a serious action to find effective remedies to the problem and secure the future in terms of natural resources and human lives.

1.1 Project Background

Pakistan is one of the major victims of global warming; massive floods of 2010 and 2012 have been recorded as the worst floods in history and are triggered by the heavy monsoon rainfalls due to Global Climate Change (Cheema *et al*., 2010). In 2010 UN summit held in Durban ranked Pakistan on top of the climate change risk's index list. Pakistan is in the top ten worst effected countries, despite of the fact that we are producing only 0.5% emissions of the total world's production. It is quite shocking but a bitter fact. Per capita consumption of fossil fuels in Pakistan is very less as compared to the modern world. This makes carbon capture and storage one of the government's top priorities along with international cooperation and mutual agreements with China, India, Russia and Iran to reduce the influx of emissions entering Pakistan. Furthermore, the military operation in

Afghanistan and on Siachin is also resulting in high rates of CO_2 emissions disturbing the climate of the region in the longer run. The intricate political set up of the area is resulting in alarming environmental degradation.

Vehicular emissions are the main CO_2 contributors in Pakistan. Each year thousands of new vehicles are introduced on the road. Industrial fuel gases are not Pakistan's main problem yet however as the country industrialize and develop; industrial emissions have been seen to increase.

This discussion has outlined one of the primary reasons that inspired the project. Another important aspect that must be highlighted here is the industrial development in the country and role of international trade. As the world progresses, international environmental standards become more stringent and trade is not possible or profitable unless communities are able to meet the standards and produce good results. Pakistan has immense potential for industrial growth. Especially in the agricultural sector, there are huge resources available in Punjab. If progress has to be made, international trade has to be strengthened and foreign collaboration encourages. This calls for solutions and technology that is better able to meet the world's demands in terms of quality. Most of the local industries in Pakistan have potential scope to go international and market their product abroad earning huge profits and getting exposure to the outside world. The global community is also keenly looking for available options to invest in Pakistan and engage in quality trade with local dealers.

Keeping this necessary development in mind, the project was designed to provide an economically feasible, yet efficient system to the local industries to meet international emission standards and obtain ISO certification to enhance trade. The newer environmental standards and legislations in recent years affect Pakistan's ability to execute international trade and survive the current economic condition prevailing in the country. There comes a need of indigenous low-cost carbon capture technology affordable to the local industries, which cannot only achieve high CO_2 removal efficiency but is also easy to operate and maintain. The technology should also be locally reproducible and independent of foreign assistance when it comes to mass production. Realizing the importance of the locally designed technology, the project was designed to put into practice a viable solution of reducing the CO_2 levels from industrial flue gases. The idea of designing and manufacturing CO_2 scrubber for reducing CO_2 levels is executed in such a way as to minimize capital and operation cost to facilitate industries. Therefore, it is directly a contributor and catalyst in economic growth of the country through reducing climatic degradation and enabling local industries in meeting international standards.

1.2 Project Statement

To engineer a Carbon dioxide scrubber that absorbs maximum CO_2 emissions with minimum energy input and proposing best solutions for the sequestered CO_2 to get benefit from it.

1.3 Objectives

This project aims to achieve the following objectives:

- Compare different concentrations of Amine Solvents Monoethanolamine (MEA) and Diethanolamine (DEA) for CO_2 capture.
- Propose cost effective, energy efficient and high performance solution for capturing and sequestering CO_2 in local industrial environment.
- Introduce the proposed Amine based CO_2 Scrubber in local industries.

1.4 Project Scope

As mentioned in the project statement in **Section 1.2**, the project scope includes construction, test runs and result analysis of an amine based CO_2 scrubber. The fabrication of the unit includes its conceptual design, construction procedures and final assembly. After the fabrication phase is completed, project will then enter the next phase and conduct test runs on the unit to study and compare CO_2 removal efficiencies of both solvents used for this study. Detailed methodology to attain the research objectives in line with the project scope are outlined in **Section** 3 of this research study. Recommendations are provided in **Section** 6 to make efficient use of the captured CO_2. Due to limited availability of time and budget, these recommendations could not be practically tested and therefore their detailed implications to the industrial settings are not included in the research scope for this study.

1.5 Milestones Achieved

Following milestones were set in the beginning of the project. The timeline presented in **Figure 3.1** was formed based on the following milestones.

- Design proposal
- Final design
- Approval of design
- Design manufacturing
- Completion of scrubber
- Design test run
- Final inspection

2. LITERATURE REVIEW

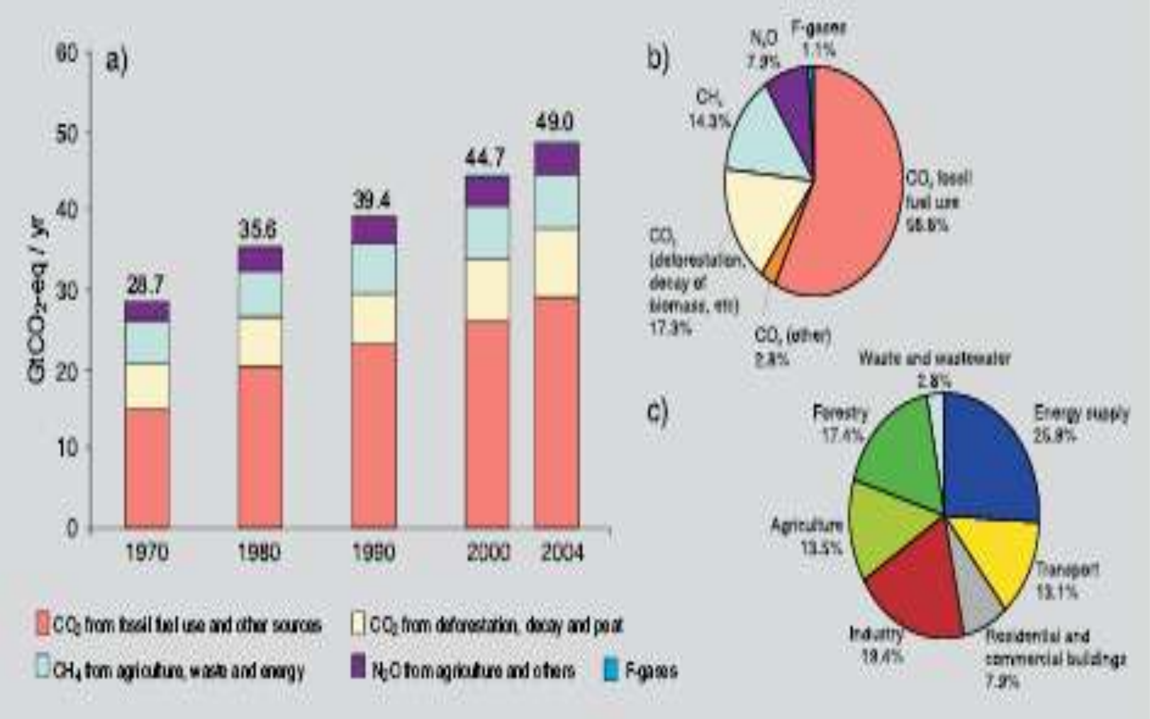
2.1 Impacts of CO_2

If the rapid consumption of fossil fuel continues to grow at the same rate, then the atmospheric CO_2 level will increase to a level double than the present levels in next 50 years. Increase in the CO_2 at a point computed by climate modeling will increase the temperature to a level, which will result in 5-meter increase in the sea levels (Mercer, 1978).

Major contribution in global warming is the presence of CO_2 gas, which is produced because of anthropogenic activities and disturbs the natural equilibrium. Increase in CO_2 levels is mainly due to the high consumption of fossil fuels like coal, natural gas petroleum and use of vehicles.

Given in **Figure 2.1**, is a graph showing percentage of greenhouse gas emissions, provided by the Intergovernmental Panel on Climate Change (IPCC).

Figure 2.1: Global Greenhouse Gas Emissions[3,4]



It further states that we have contributed approximately more than 6000 million metric tons of CO_2 emissions into the atmosphere since the very start of industrial evaluation. A variety of facts and figures is present in literature, which shows the most contributing country of CO_2 emissions.

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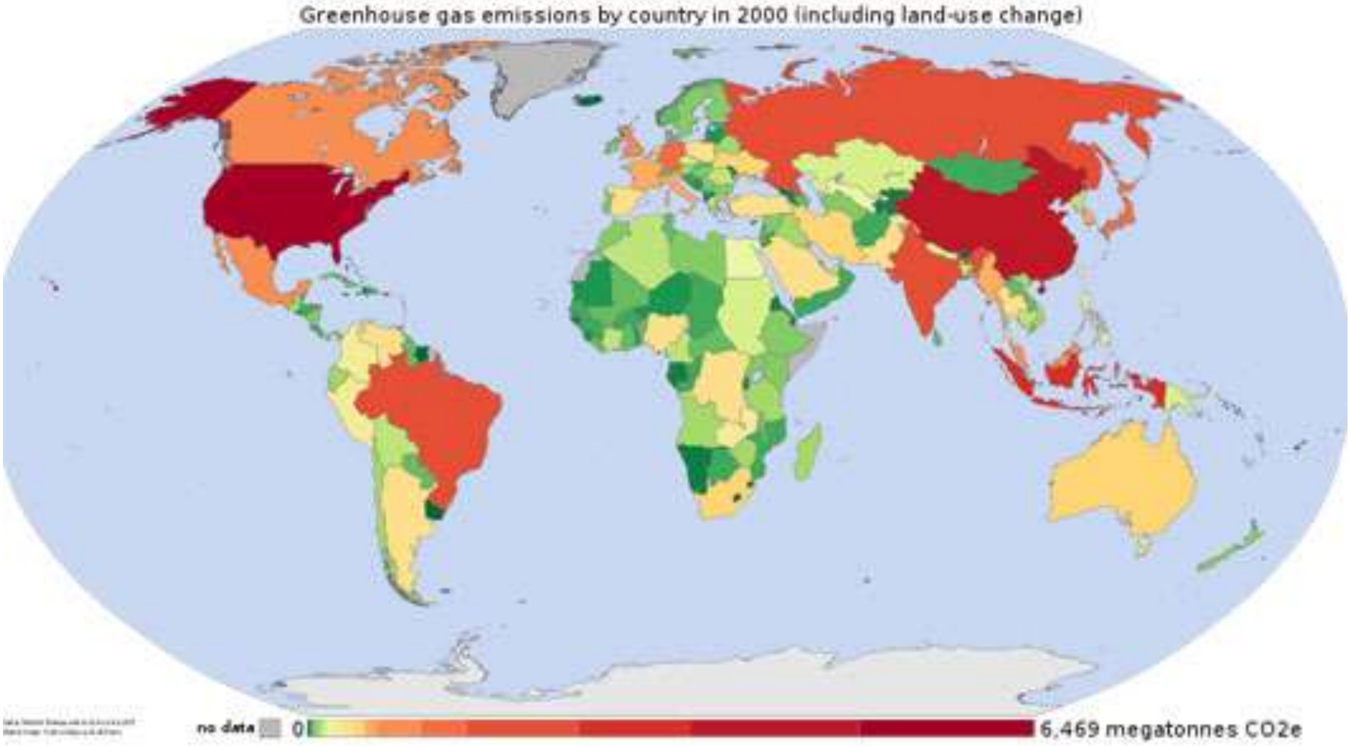
[3] Intergovernmental Panel on Climate Change (IPCC), IPCC Fourth Assessment Report: Climate Change 2007, http://www.ipcc.ch/publications_and_data/ar4/syr/en/spms2.html, Accessed on **17 December 2013**.

[4] (a) Global annual emissions of anthropogenic GHGs from 1970 to 2004 (b) Share of different anthropogenic GHGs in total emissions in 2004 in terms of carbon dioxide equivalents (CO_2-eq). (c) Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO_2-eq. (Forestry includes deforestation).

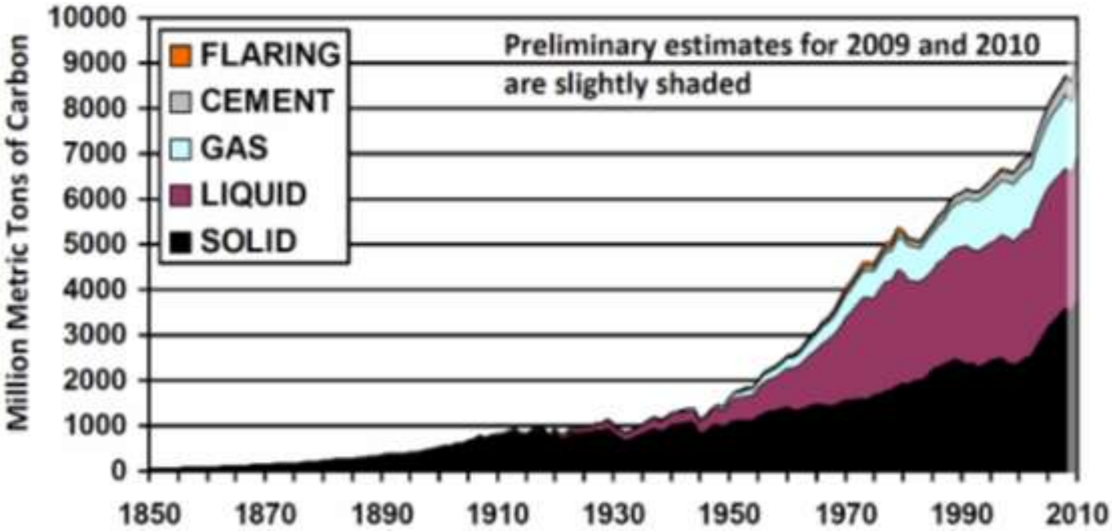
Figure 2.2: Global Greenhouse Gas Emissions[5]



[5] Mother Nature Network (MNN), http://www.mnn.com/earth-matters/climate-weather/stories/half-of-greenhouse-gases-emitted-by-5-nations, Accessed on **17 December 2013.**

In a recent report published in Daily Kos group under Climate Change section, it is mentioned that CO_2 emissions rate grew 3.1% per year from 2000-2012. Due to this severe increase in CO_2 emissions rate approximate increase of 2 degree Celsius is expected. In the period of 1990-2012 growth rate was 2.2%. It is an exponential growth rate. If the growth continues at same rate then rise of 4-6 degree Celsius is expected in future. **Figure 2.3** shows fossil fuel and cement emissions over the past years.

Figure 2.3: Fossil Fuel and Cement Emissions[6]



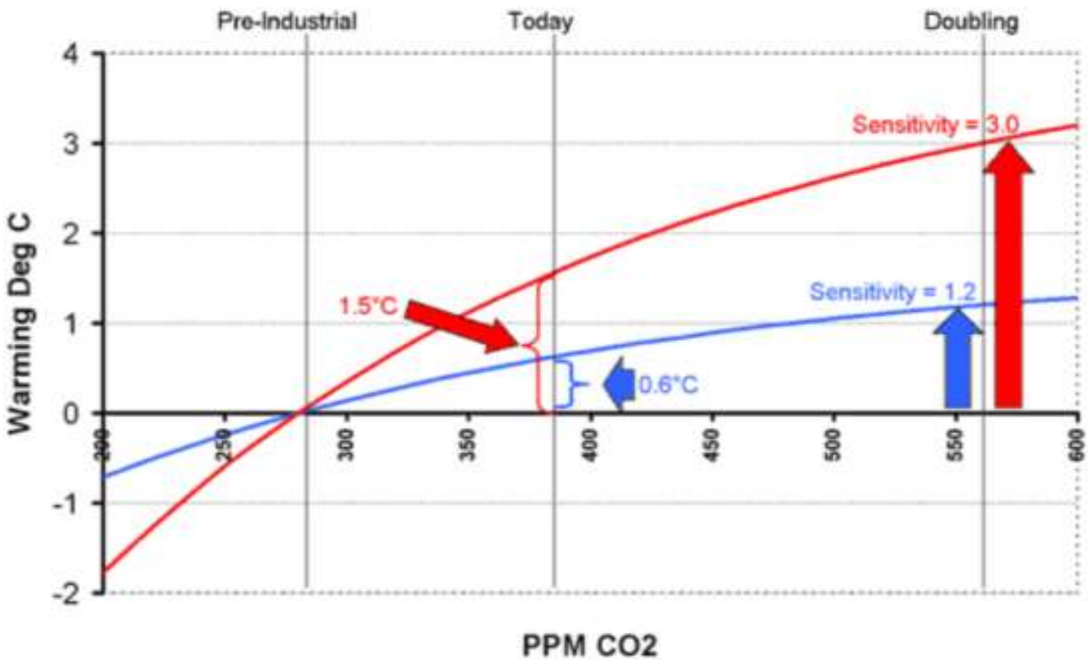
Second major reason of increasing CO_2 level in atmosphere is the rapid increase in deforestation rate around the globe. Forests are the natural sink for the absorption of CO_2, which, we are depleting at a very high rate.

According to a report by Worldwide Fund (WWF), Pakistan is currently occupying 2.5% forest cover. In addition to that, forest is being depleted at a rate of 2.1%. To meet international commitments for reaching Millennium Development Goals (MDG), to which Pakistan is a signatory, increasing forest cover from 2.5% to 6% will be difficult if deforestation at such drastic rate continues. More than 61,000 hectares of forest have been converted to non-forest use since the origin of Pakistan. Rise in global temperatures is one of the consequences of high deforestation rate. The warming potential of CO_2 can

[6] Carbon dioxide Information Analysis Center (CDIAC), http://cdiac.ornl.gov/trends/emis/prelim_2009_2010_estimates.html, Accessed on **17 December 201.**

be expressed as climate sensitivity. The trends of climate sensitivity to CO_2 over the last two years are shown in **Figure 2.4**.

Figure 2.4: Trends of Climate Sensitivity to CO_2[7]



Due to global warming effect of CO_2, it is very important to find a method for sequestrating it to a level that is not harmful for the atmosphere along with the advancement in the industrial revolution.

2.2 Techniques Used for CO_2 sequestration

Different techniques, which are being employed for the sequestration of CO_2, are

- Geological storage
- Ocean storage
- Mineral storage
- Energy requirements

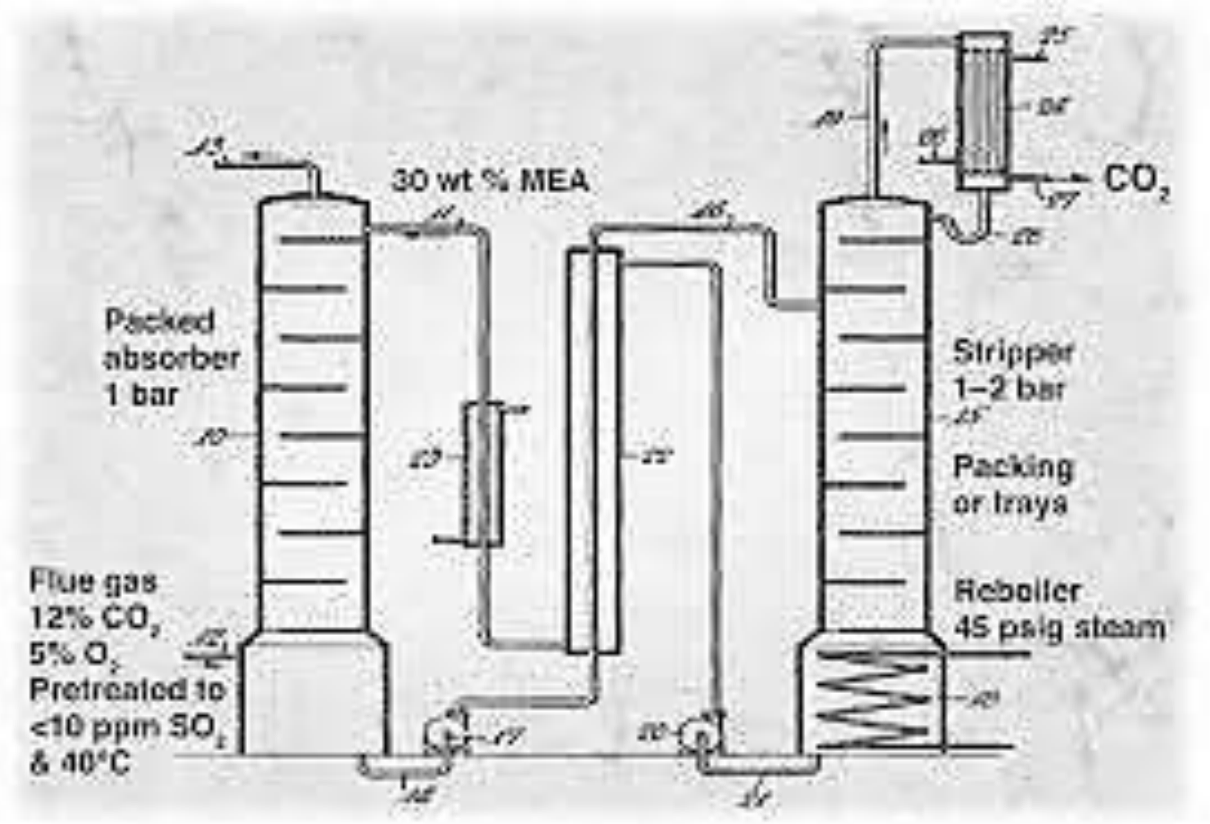
[7] Warren Meyer, Climate sensitivity- lowering the IPCC "fat tail",http://wattsupwiththat.com/2011/11/09/climate-sensitivity-lowering-the-ipcc-fat-tail/ Posted **on 9 November 2011**. Accessed on **17 December 2013.**

Other techniques being used include CO_2 scrubbing by means of different chemicals. Scrubbers are very popular these days for CO_2 emission control from industrial stack.

2.3 CO_2 Sequestration using Amine scrubbing technique

Amine scrubbing is a very old technique being used since 1930s (Rochelle, 2009). This technique was first deployed for the separation of CO_2 from natural gas and hydrogen. It is a stout sequestration technique and can be easily used for large scale scrubbing of CO_2. The technique is demonstrated in **Figure 2.5**.

Figure 2.5: Amine Scrubbing Process by Bottoms, R.R. (1930)



This is the first amine scrubbing process unit invented by R. R. Bottoms in 1930. According to the International Journal of Greenhouse Gas Control (2008), there has been considerable advancement in the carbon capture technologies through these years. There are three main processes for the carbon capturing from coal fired power plants, namely:

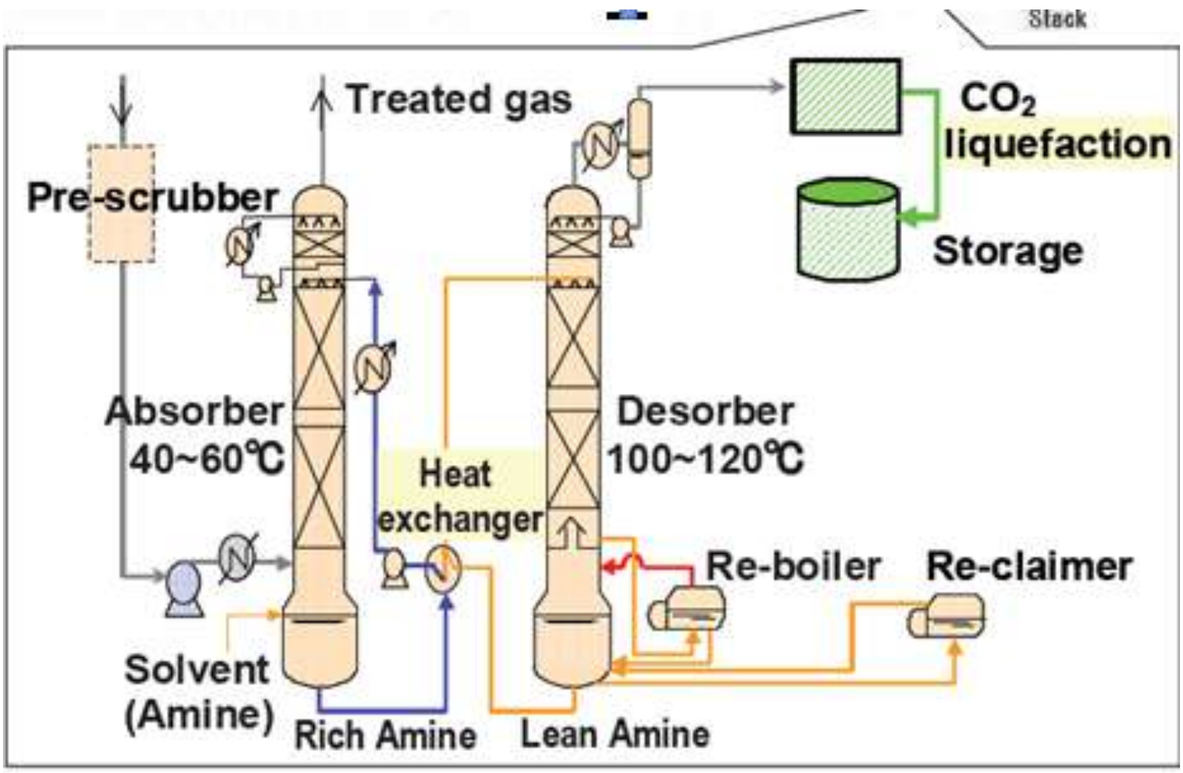
Pre-combustion ⟹ **Combustion** ⟹ **Post combustion**

Many alterations have been made in the conventional MEA scrubber process flow sheet system when compared to the first one developed by Bottoms.

According to the Hitachi's Carbon Dioxide Scrubbing Technology with New Absorbent for Coal fired power plants Paper 60, Hitachi has developed new technology using many different amines. More than 30 amines were combined with other solvents for obtaining higher efficiencies.

These innovations are being done for improving the efficiency of CO_2 capturing and lowering the energy consumption by the scrubber plant, in short, making the system effective for large-scale usage. The **Figure 2.6** shown below is the process flow diagram presented by Hitachi after modification of the conventional process.

Figure 2.6: Hitachi's Post Combustion CO_2 capture process



Using this process flow sheet Hitachi obtained the removal of 90% CO_2 from stack emissions using different combinations of amines and other additives. Other than Hitachi, there are many available modifications for improving efficiency of scrubbing process.

In the system proposed in this study, focus has been on changing configuration of the scrubber design to get better efficiency. It is cost effective and simple, using this configuration pilot scale experiments have been designed and results are deduced. The new configuration gives efficient removal of CO_2 from flue gas emissions. Results have shown removal of approximately 92-94% CO_2.

3. METHODOLOGY

As this research is a scientific endeavor to understand the process of CO_2 sequestration using Amine solvents, quantitative analysis is applied in its methodology. The data collected from months of experimentation on the prototype is recorded and has undergone analysis to plot efficiencies of different solvents. The main reason for selecting quantitative analysis for this study was the nature of primary data collected for the study. As the data is numerical and requires tabulated results, therefore quantitative analysis using Microsoft Excel were deemed necessary. This analysis also helped in accurate conclusions about the performance of solvents and the manufactured prototype. According to literature, quantitative analysis is utilized by researchers where numerical data is involved and is usually a feature of scientific and tangible researches where such analysis can produce authentic and accurate results whereas qualitative or phenomenological methodology is applied where research addresses an abstract or intangible topic and requires secondary research to reach conclusions.

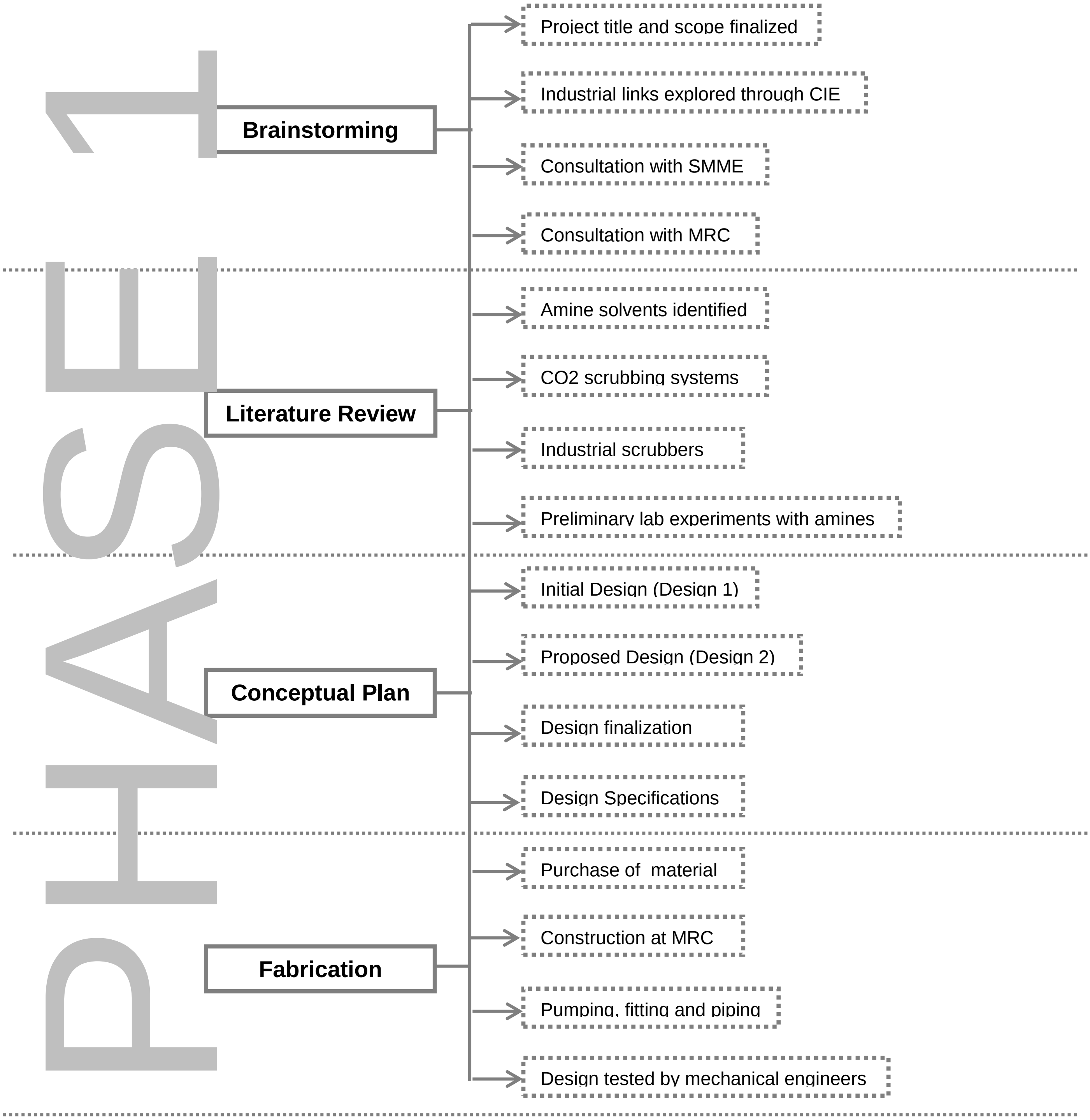
Where necessary, qualitative comparisons have been made with information available in published and authentic sources. Secondary information has also been used to validate and justify the results of this research. Therefore, qualitative analysis tool has been used as a complimentary means to further authenticate and validate the results of this research.

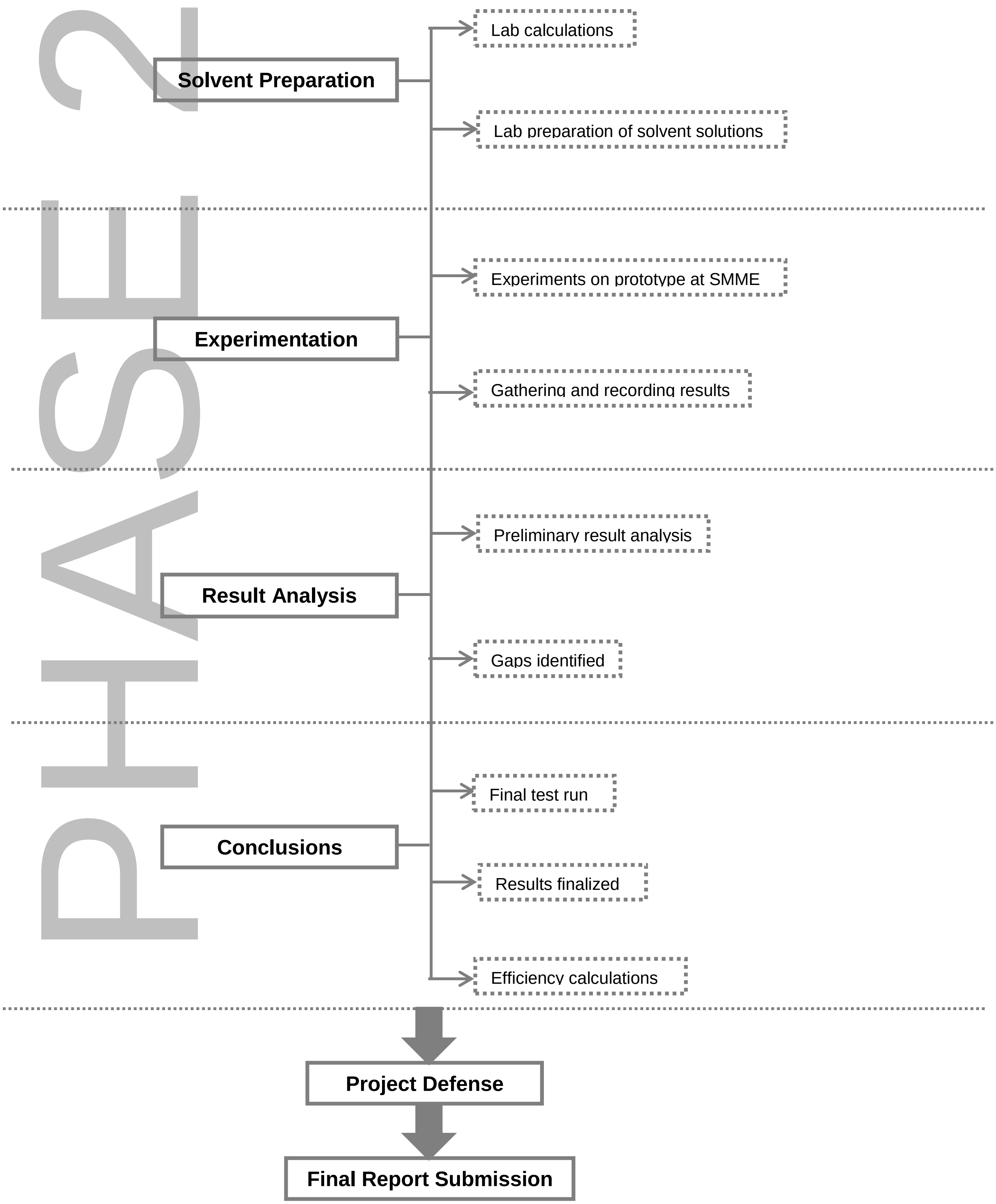
Primary data comes from experiments conducted on the prototype manufactured in phase 1 of this research i.e. fabrication of the prototype. The data has been collected on daily basis and is recorded in tabulated form. Data collection form is attached as **Appendix A** with this report. The complete duration of data collection ranges over three months and 13 days excluding weekends and public holidays. Temperature, time, and CO_2 concentrations at every time step were recorded by researcher conducting the experiment. A digital copy of these results obtained from the Emission Gas Analyzer software by Taylor is also available with the researchers. Emissions of the source were recorded separately to make comparisons and calculate efficiencies later.

Secondary information comes from published literature and industrial reports that are already employing the amine based scrubbing techniques. It has been confirmed by the researchers to reference and where necessary obtain permission from respective owners before using any secondary research quoted in this study. Comparisons and supporting arguments have been given to justify the results produced by this research work.

In order to accomplish the project, tasks were grouped into two major phases. A project timeline was devised keeping in mind the time constraints. Each deliverable of this timeline was assigned to certain members of the team who were responsible for the smooth execution of the deliverable. The timeline was devised after consultation with the team, the supervisor, mechanical engineers and specialists. It is illustrated in the flowchart in **Figure 3.1**. This study was conducted in collaboration with School of Mechanical and Manufacturing Engineering (SMME) and Manufacture Resource Center (MRC). Both SMME and MRC are constituents of National University of Sciences and Technology (NUST).

Figure 3.1: Project Timeline




PHASE 2
Solvent Preparation
Lab calculations
Lab preparation of solvent solutions
Experimentation
Experiments on prototype at SMME
Gathering and recording results
Result Analysis
Preliminary result analysis
Gaps identified
Conclusions
Final test run
Results finalized
Efficiency calculations
Project Defense
Final Report Submission

3.1 Phase 1: Fabrication of the Prototype

As discussed above, the project deliverables can be divided into two major phases which will be discusses in the following sections.

Phase 1 may further be subcategorized into the following tasks:

- Preliminary consultations and scoping
- Establishing the context of the project through baseline studies and literature review
- Conceptual plan for project fabrication and experimentation
- Implementation of the conceptual plan

3.1.1 Brainstorming

Several brainstorming sessions were convened in order to identify the need for the project discussed in **Section 1** of the report. The primary purpose of organizing these sessions was to draw useful conclusions about the most significant problems facing the country and devise an approach to address one or more of these. Several ideas were put up over the course of these sessions, which included ideas from the renewable energy sector, waste management, waterlogging and salinity among others.

After shortlisting plausible ideas that could be pursued within given time and budget, consultations with field specialists, supervisors and industrialists were done to understand the nature of problems. The Center of Innovation and Entrepreneurship at NUST (CIE) was contacted for consultation and industrial links. Through these consultations and through interaction with PEPSICO Lays Plant in Lahore, it was decided that indigenous carbon sequestration technology is the need of the hour and can result in many potential benefits for the Pakistani industries and Small and Medium Enterprises (SMEs).

3.1.2 Literature Review

Once the project scope and objectives were finalized after consultation and brainstorming sessions, extensive literature review was conducted to gain an in-depth understanding of the issue. The literature review and its findings have been discussed in more detail in

Section 2. This exercise also helped and formed basis of the next project deliverable i.e. conceptualization of the prototype and its working.

3.1.3 Conceptual Plan for Ultra Magnus (UM)

The prototype was named as 'Ultra Magnus' (UM). Conceptualization of its working model was a rigorous task of planning, discussion, feedback, consultations and revising the plans. This task was also responsible for the major time span in Phase 1. From literature review and case studies of industries outside Pakistan, the initial design (Design 1 in **Figure 3.2**) was proposed for review by supervisor and specialists.

This design, although functional, proved to be costly due to the nature of cylindrical units, two pumps and cost of support units. It was decided that the design should be revised to make maximum use of gravitational fluid flow and minimum support for the unit.

This led to a revised design 'Design 2' shown in **Figure 3.3**. The main features of this design were that it reduced the cost, provided an innovative solution to increase volume and efficiency of the system. More details on the comparison and specifications of both designs are provided in **Section 3.2.1**.

Absorber and Desorbed unit in the selected design are pyramid shaped. The pyramid shape with a square base of 7 inches length, in the absorber unit helped provide the necessary contact time for the reaction to occur between CO_2 and solvent. Flue gas with minimal CO_2 is converged and removed from the top.

The pyramid shape with a square base of 6 inches length, in the Desorber unit aided in achieving and maintaining a temperature of 120 °C in the Desorber. Solvent is converged at the outlet in the bottom and passes through the recycle line before being sprayed again at the absorber unit.

For the scrubber to run continuously, recycled solvent will not meet the required MEA demand at inlet. Therefore, in addition to this, fresh solvent is added in a limited quantity to make the system run continuously. Design specifications of absorber and Desorber are given in **Figure 3.4**. A comparison of the initially proposed design and the final design is illustrated in **Table 3.1.**

The design was eventually finalized after consultations with mechanical engineers, project supervisor and technical specialists in the field of environmental technology. To further increase performance of the unit, pump and piping features were altered. Shape of the absorber and Desorber unit was modified as well keeping in mind the convergence of liquid and gas at container's ends. Comments on the design were addressed and amendments were made in light of expert opinion. The final design approved for fabrication is shown in **Figure 3.5**.

Shown in **Figure 3.6** and **Figure 3.8** are the schematics of Absorber and Desorber unit. Showerhead in the absorber unit allows a flow rate of 0.2 liter/second to be maintained. Heating rod in the Desorber unit is suspended by means of metal rods.

Figure 3.7 shows cross-section of the Absorber. Design has been modified to remove extra pumps and valves being used to pump the MEA and CO_2 solution from absorber to Desorber and in recycling back of MEA. Showerhead is being used for showering monoethanolamine from the top. CO_2 is being supplied from the bottom of the absorber unit.

Figure 3.2: Initial Proposed design for Ultra Magnus (Design 1)

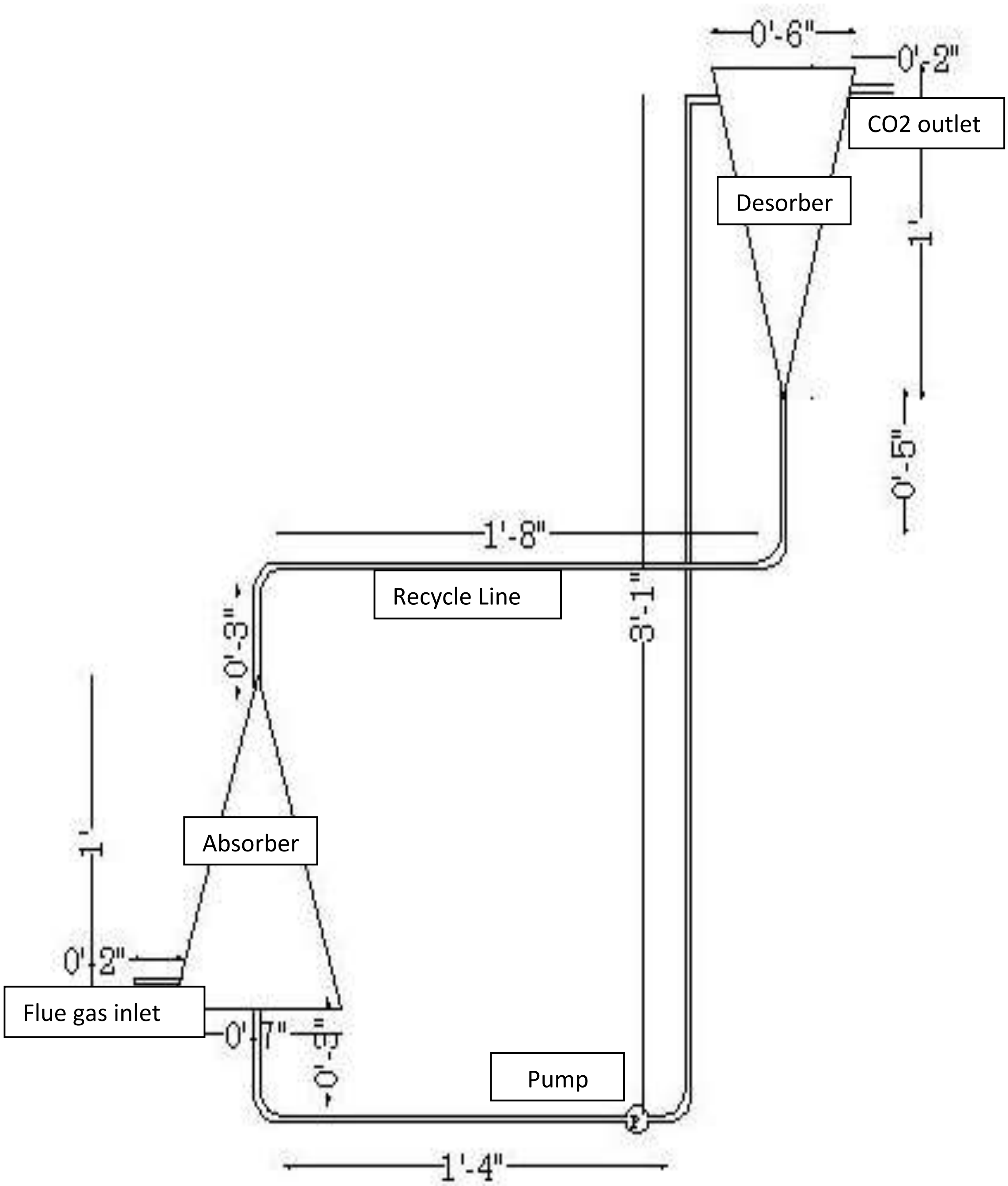


Figure 3.3: Alternate Design Proposed for Ultra Magnus (Design 2)

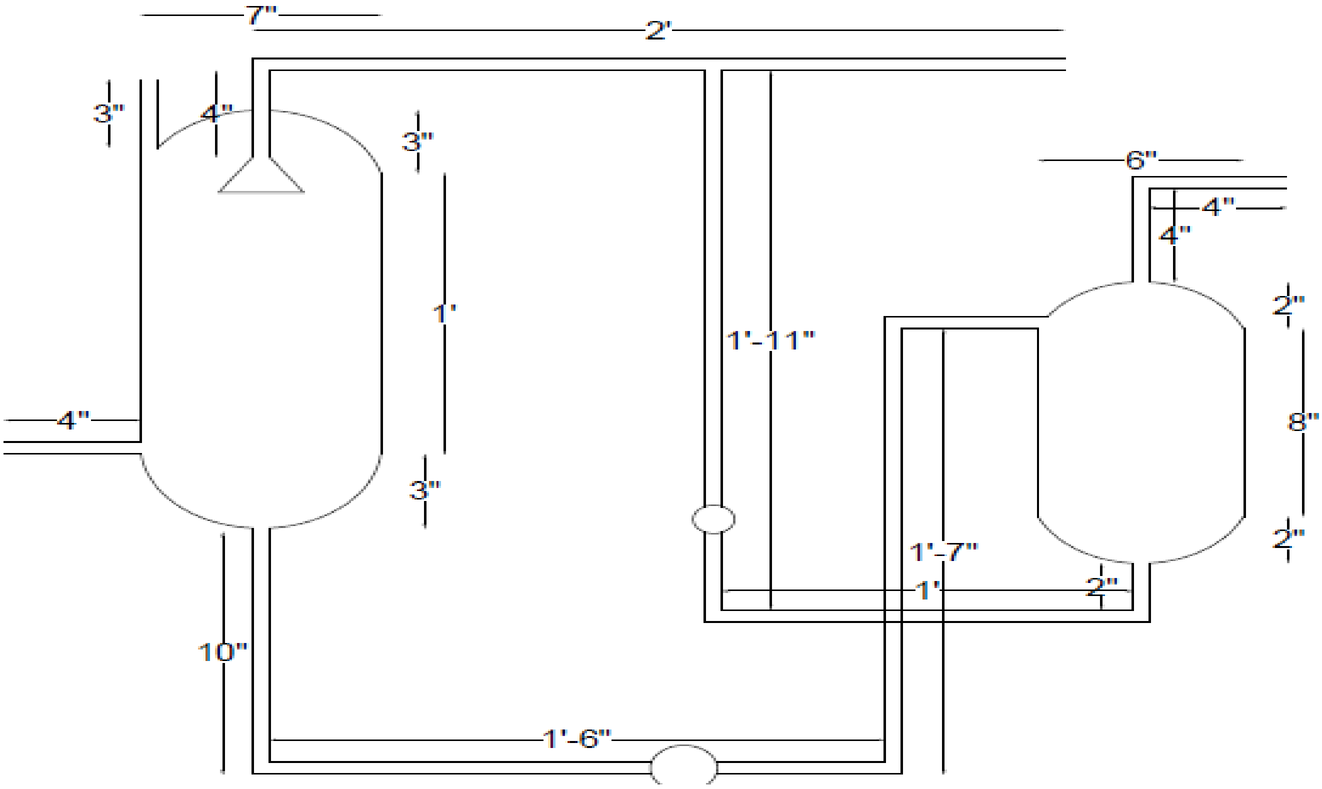


Figure 3.4: Absorber and Desorber Specifications

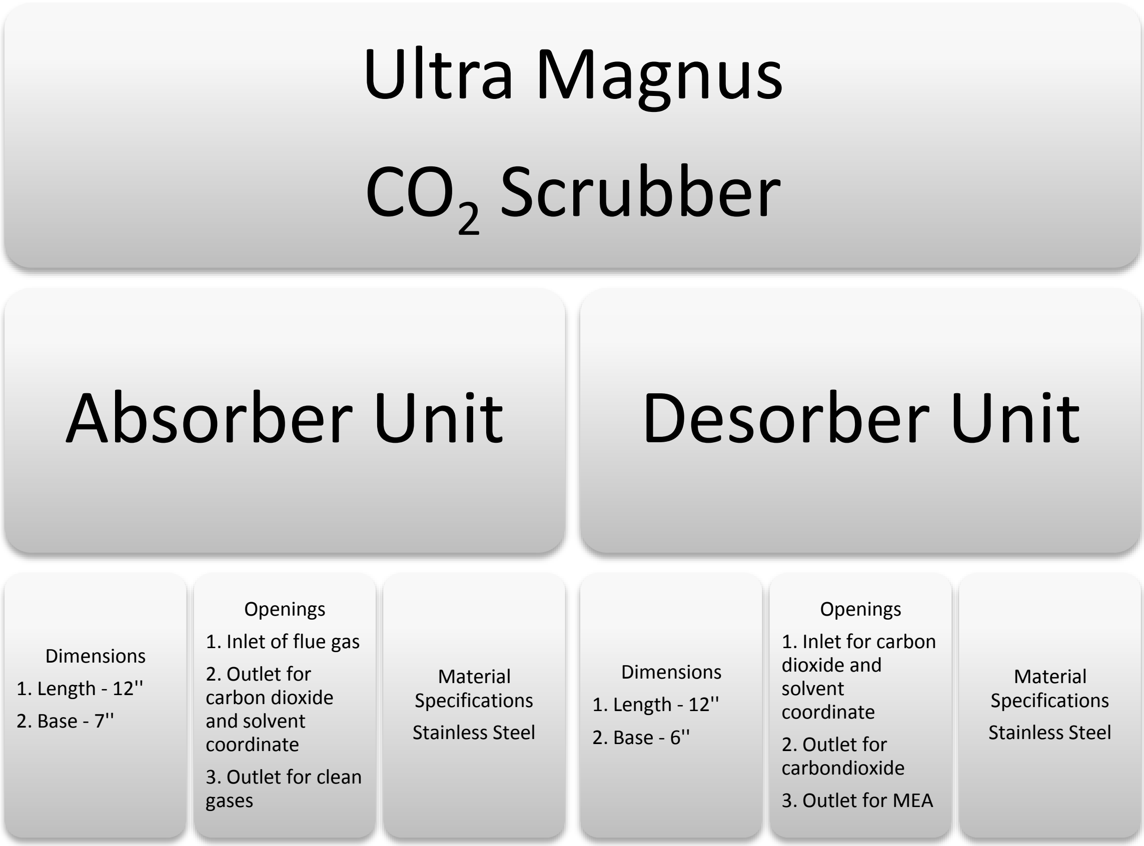


Table 3.1: Comparison of Design 1 and Design 2

Specification	*Design 1*	*Design 2*
Components:	Pump (1) Tetrahedral Pyramid Tanks (2) Valves (3)	Pumps (2) Cylindrical Tanks (2) Valves (2)
Capital Cost:	More cost effective as one Pump is used.	Less cost effective as two pumps are used
Construction:	Easier construction of tetrahedral stainless steel pyramids	Complex construction of stainless steel cylinders
Surface Area:	653 in^2	564 in^2

Figure 3.5: Final Design for Ultra Magnus

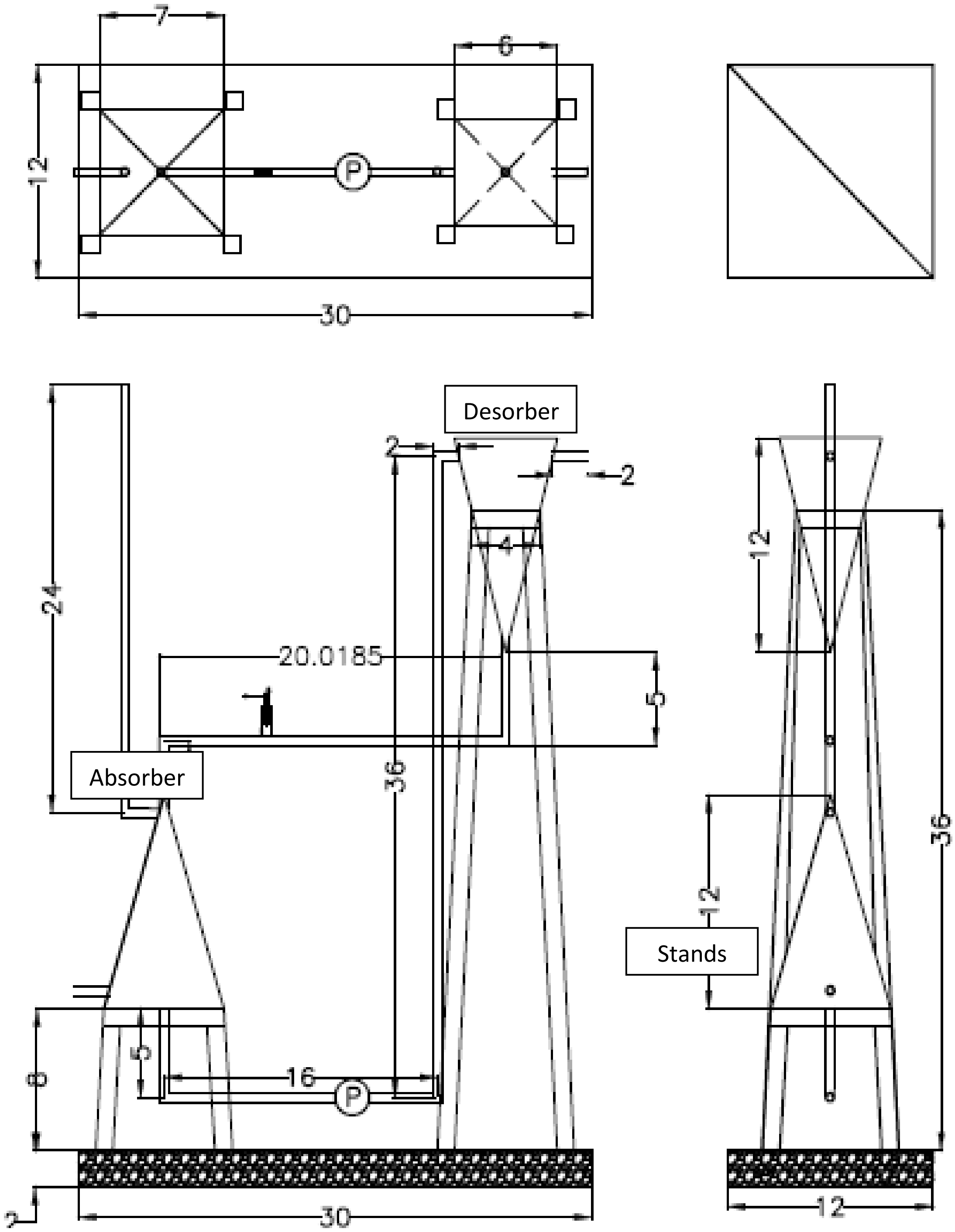


Figure 3.6: Structure of the Absorber Unit

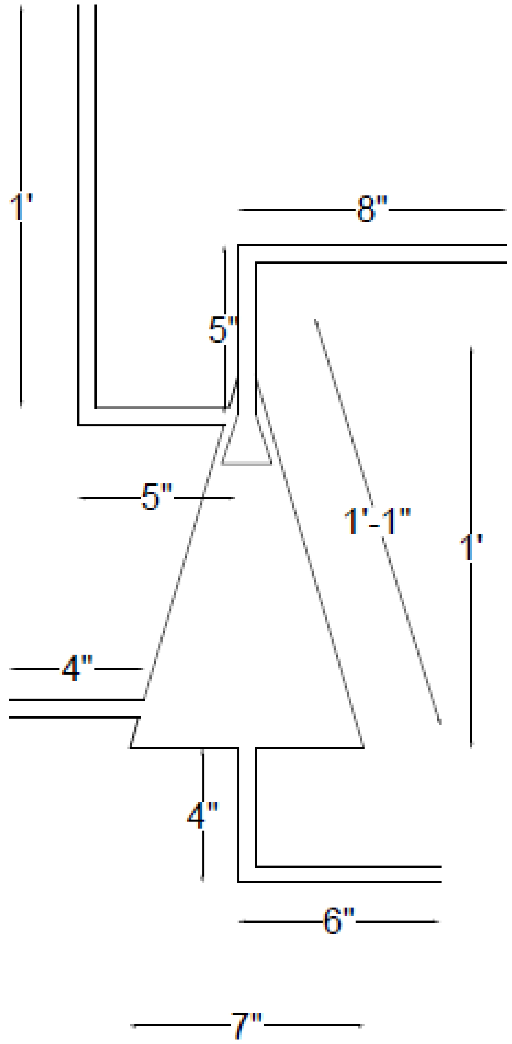


Figure 3.7: Internal Structure of the Absorber Unit

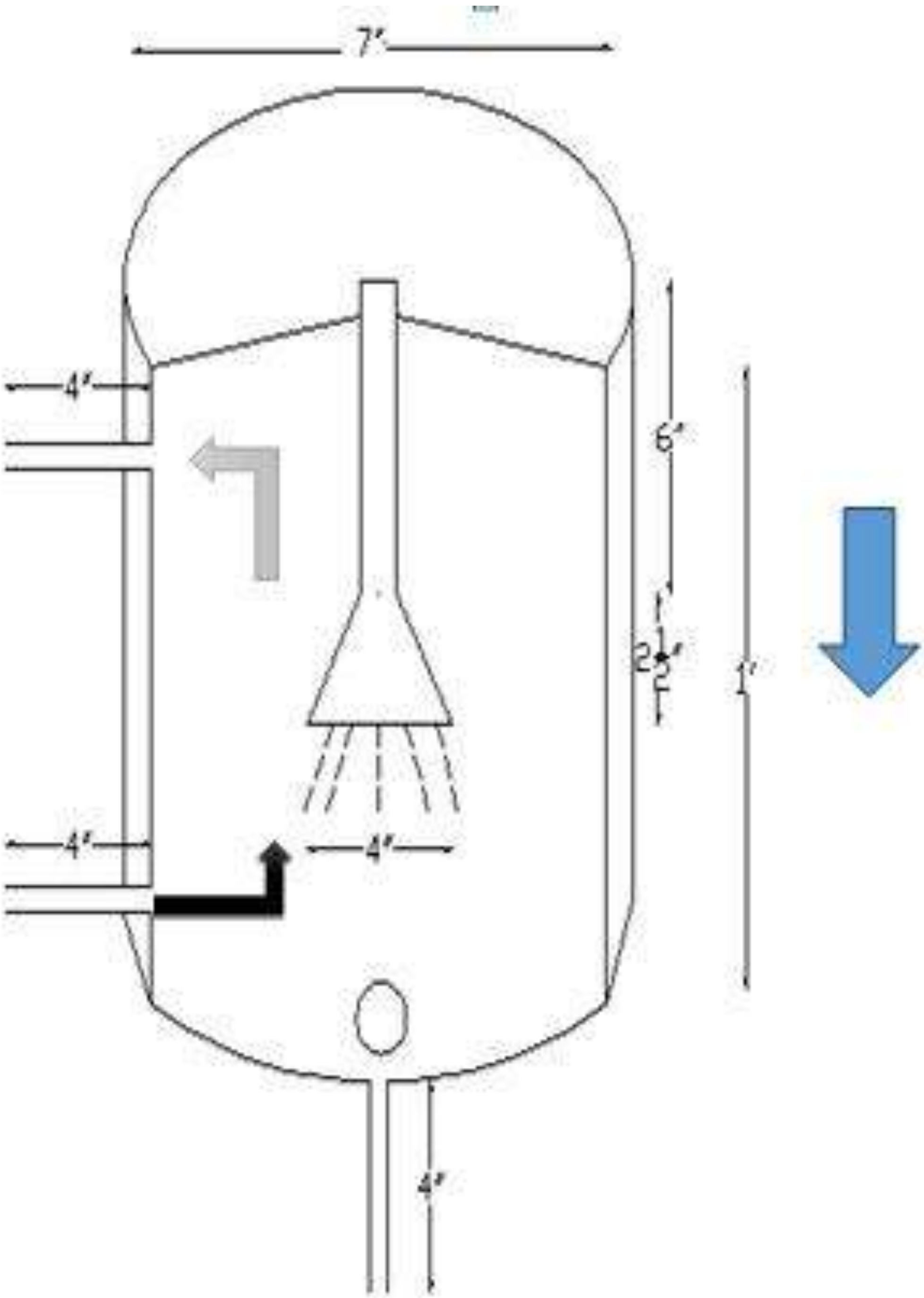
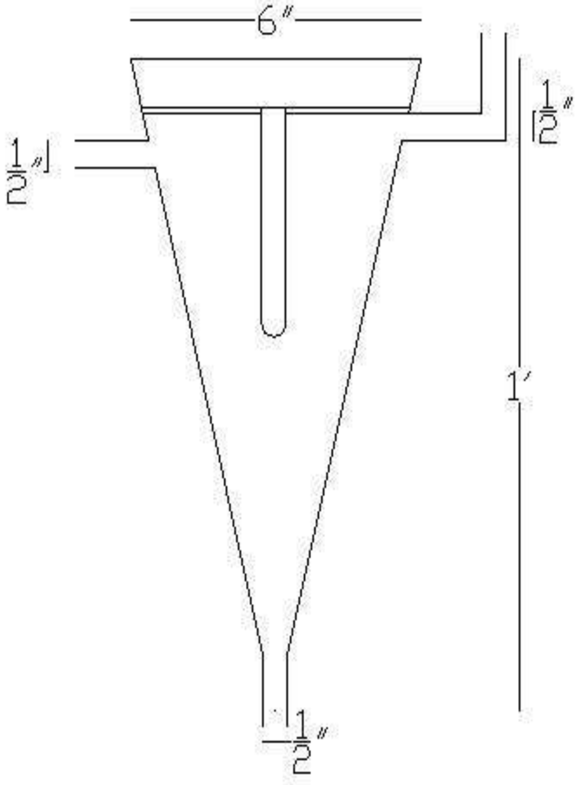


Figure 3.8: Structure of the Desorber Unit



3.1.4 Fabrication of UM

Once the design and its specifications were finalized and approved by supervisor and mechanical engineers, the project entered the fabrication phase, which started with purchase of project material. A Billing of Material (BoM) was prepared for the overall financial expenditure and capital costs associated with components purchase. Indigenous resources were used for fabrication of the prototype. A detailed list of materials/components along with their specification and quantity is mentioned in **Table 3.2.**

Fabrication of UM Absorber and Desorber units was done at the Manufacturing Resource Center (MRC) at NUST. The piping, fitting and buffing procedures were completed at workshops outside NUST after Absorber and Desorber were fabricated. The final design is shown in **Figure 3.9.** Phase 1 attained competition with the fabrication of UM.

Figure 3.9: Prototype Ultra Magnus

Table 3.2: Details of Material Used in Construction of Ultra Magnus

S. No	*Component*	*Specification*	*Size*	*Quantity*
1	**Pipe**	Galvanized Iron (GI)	Diameter (1/2 in)	12 ft.
2	**Stainless Steel (SS) Sheets**	SWG 16.	2 ft. x 4 ft.	1
3	**Rectangle Pipe**	SWG 16	2 in x 5/4 in	14 ft.
4	**Elbows**	Galvanized Iron (GI)	Diameter (1/2 in)	24
5	**Tee**	Galvanized Iron (GI)	Diameter (1/2 in)	8
6	**Ball Valve**	Galvanized Iron (GI)	Diameter (1/2 in)	3
7	**Heating Rod**	Max Temp 120^{o}C	-	3
8	**Pump**	Reciprocating	Flow Rate (0.2 m^3/s)	1
9	**Ply Wood**		36 ft. x 16 ft.	1

3.2 Phase 2: Experimentation and Result Analysis

In parallel to the fabrication activity at MRC, experimentation and solution preparation started at the IESE laboratory at NUST. This section will describe the methodology adopted for experimentation, analysis of results and explanation of the working of UM.

3.2.1 Introduction to Solvents

After literature review and consultations with experts, following solvents were selected for this study:

Monoethanolamine (MEA)

The chemical used to absorb CO_2 is MEA, which is an alkanolamine, which absorbs CO_2 very well at temperatures above 250^oF. Pure MEA has normality around 15.8, but in the Scrubber MEA is diluted to about 4.0N. MEA has a very strong ammonia-like odor and is considered a hazardous material. During the early years of CO_2 Scrubber technology, MEA would last for less than 200 hours before degrading and becoming ineffective. Today, chelating agents are used to prolong the life of MEA. This chelated MEA can operate for over 1000 hours before having to be replaced. This limits the negative health effects associated with the chemical. Today, testing is taking place to improve scrubber technology in such a way that chelating agents are no longer necessary, in order to simplify the Scrubbing process.

The chemical reactions involving MEA are shown in the following Figure (**Figure 3.10**).

Figure 3.10: Reactions taking place in aqueous system of MEA and CO_2

$$H_2O + MEA^+ \longleftrightarrow H_3O^+ + MEA$$

$$2\,H_2O \longleftrightarrow H_3O^+ + OH^-$$

$$H_2O + HCO_3^- \longleftrightarrow H_3O^+ + CO_3^{2-}$$

$$CO_2 + OH^- \longrightarrow HCO_3^-$$

$$HCO_3^- \longrightarrow CO_2 + OH^-$$

$$H_2O + CO_2 + MEA \longrightarrow MEACO_2^- + H_3O^+$$

$$MEACOO^- + H_3O^+ \longrightarrow H_2O + CO_2 + MEA$$

The major advantage of using amines is that, it is not consumed and can be recycled in an ideal setting. This study uses 30 and 20 percent by weight of MEA and DEA. Comparison is drawn of the results obtained by using different type and concentration of amine.

Diethanolamine

Diethanolamine (DEA) is a clear, colorless, hygroscopic liquid with a mild ammoniac odor at temperatures higher than room temperature. At room temperature, the product is a white, crystalline solid. It is a weak base and it is not as corrosive as MEA. Being less corrosive is the reason that it is used for carbon sequestration. It is not as strong as MEA so its efficiency is quite low. Hence, it is not recommended for commercial sequestration of CO_2.

Chemical reactions in the absorber involving DEA solvent are given in **Figure 3.11**.

Figure 3.11: Reactions taking place in aqueous system of DEA and CO_2

$$H_2O + MEA^+ \longleftrightarrow H_3O^+ + MEA$$

$$2\ H_2O \longleftrightarrow H_3O^+ + OH^-$$

$$H_2O + HCO_3^- \longleftrightarrow H_3O^+ + CO_3^{2-}$$

$$2\ H_2O + CO_2 \longleftrightarrow H_3O^+ + HCO_3^-$$

$$H_2O + MEACOO^- \longleftrightarrow MEA + HCO_3^-$$

3.2.2 Experimentation

Once the solvents were prepared and the unit was fabricated, experimentation phase commenced. The total period of experimentation excluding weekends and public holidays is three months and 13 days. This time was sufficient to obtain accurate results for calculation of prototype's efficiency.

Working of UM

A Honda CD70 2005 model motor cycle model was used as fuel emission source.[8] The five Gas Emission Analyzer (GEA) at SMME from Taylor (U.S.) was used to analyze the CO_2 during experimentation. The GEA is shown in **Figure 3.12**. Example output from the analyzer, used for recording experiment results is shown in **Figure 3.13**.

CO_2 concentration in terms of percentage was recorded for the fuel source. Average concentration of fuel source emissions recorded over three months is 6%. The motor cycle exhaust gases will be called flue gases (term used for industrial exhaust gases) for the purpose of this study. The emission analyzer showed the following major gases as constituents of the exhaust gases (given with their average concentrations):

- Carbon dioxide (6%)
- Nitrogen dioxide (1000 ppm)
- Nitrous oxide (700 ppm)
- Ozone (0.1%)
- Oxygen (0.1%)
- Water vapors (7%)

Flue gases were then allowed to enter the Absorber through the inlet (**Figure 3.7**). Solvent solution was showered from the top of the unit. A reaction time of five to ten minutes was allowed to absorb the flue gas CO_2 into the amine. Temperature in the Absorber was noted to increase due to the chemical reaction and complex formation in the Absorber.

Readings were taken for the CO_2 concentration at every minute interval. Due to the small size of the prototype and less quantity of incoming flue gases, absorption was relatively quick and after an average 12 minutes, CO_2 concentration in the Absorber became almost constant.

Length of the unit has been chosen keeping in mind that adequate contact time for the reaction to be efficient is provided. CO_2 initiated degradation begins with the formation of 2-oxazolidone. 2-

[8] Motorcycle emissions for the manufactured prototype were suitable because the prototype is approximately 1/1000 times less in size compared to an actual industrial unit. A large fuel source was therefore, not recommended for this study.

oxazolidone reacts with another MEA molecule to form N-(2-hydroxyethyl)- ethylenediamine via intermediates of N,N′-di(hydroxyethyl)urea and 1-(2-hydroxyethyl)-2-imidazolidone (Strazisar *et al*., 2012).

The complex formed according to the equations mentioned in **Section 3.2.1** of this report, travelled through the pumping line and was pumped to the Desorber Unit where a temperature of 120^0C was pre-set. At this temperature, solvent-CO_2 complex formed in the Absorber is thermally degraded to yield the Amine and capture CO_2. The clean flue gases were released into the atmosphere through the outlet shown in **Figure 3.7** while CO_2 obtained because of thermal degradation was captured and passed through the GEA to validate results. The amine solvent was recycled back through the recycling line into the Absorber.

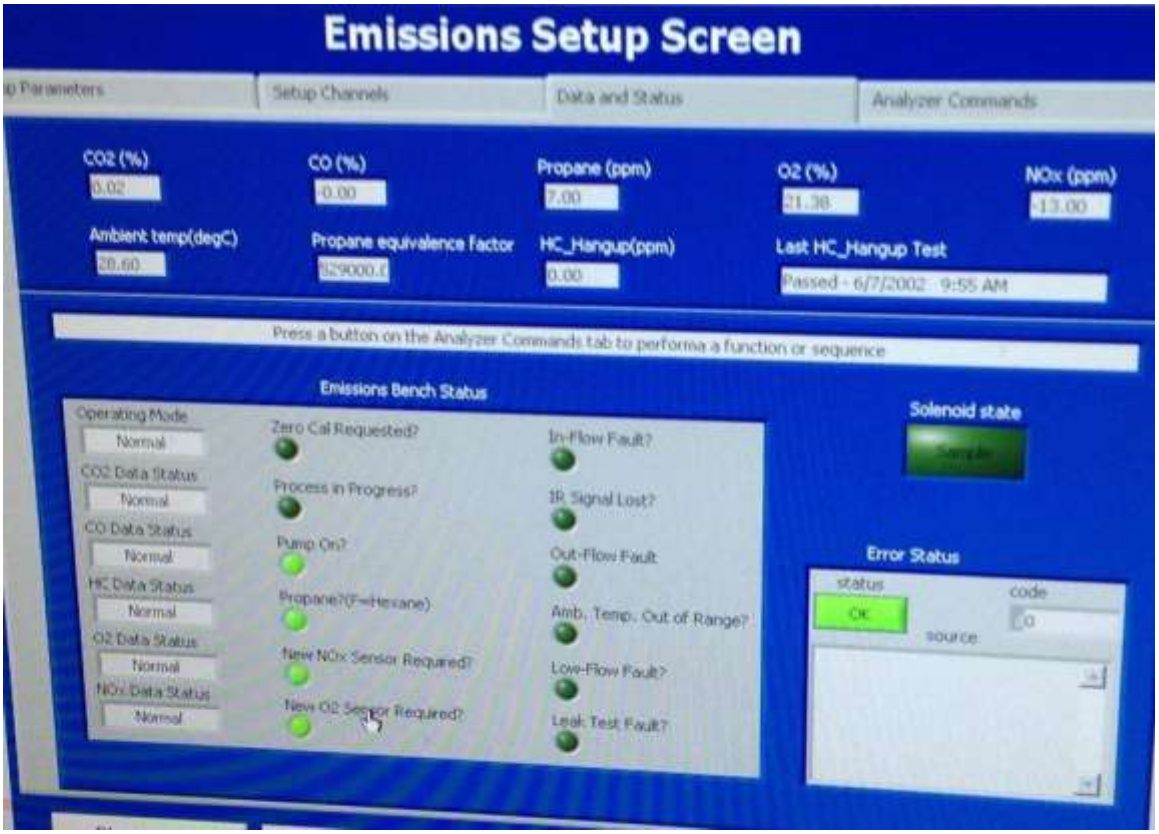
Record of Experiment Data

Experiment data was thoroughly checked and recorded in a proper format developed exclusively for this study. The record form is attached in **Appendix A**. Following information was recorded for each experiment:

- Source emission CO_2 concentration
- Ambient temperature
- Absorber temperature (at every minute interval)
- Absorber CO_2 (at every minute interval)
- Any comments or observations made by the experimenter.

Figure 3.12: Taylor's Five Gas Emission Analyzer (GEA) at SMME

Figure 3.13: Example Output from Taylor GEA



3.2.3 Result Analysis

Results were analyzed on fortnightly basis to study the progress of research. Where gaps were identified or experiment observations were improperly recorded, further experiments were conducted. With the passage of time, it was observed that corrosion is a major issue in the system and further literature studies were done in order to address the problem. Another problem of amine absorption technique, identified in the research was that it degrades over time by producing by-products, which decrease efficiency of CO_2 capture. Chemical absorption can be improved by limiting or eliminating degradation caused by oxygen, NO_x and SO_x in the flue gas. It can be done by using lower amine concentrations, distilling amine before recycling and continuously adding fresh supply. These remedial measures, however, result in increased material use, energy requirements and higher maintenance costs (Strazisar *et al.*, 2012). The results and conclusions are further discussed in through detail in **Section** 4 and **Section** 5 respectively.

4. RESULTS AND DISCUSSION

Test runs were conducted by using the prototype constructed. MEA and DEA percentages were varied. Four parameters were analyzed, when MEA concentration is 30% and 20% and when DEA concentration is 30% and 20 %. Based on the amine concentrations used for testing efficiency of solvents, four scenarios were developed, each with different solvent concentration. These scenarios and results obtained after running them are discussed in detail as under:

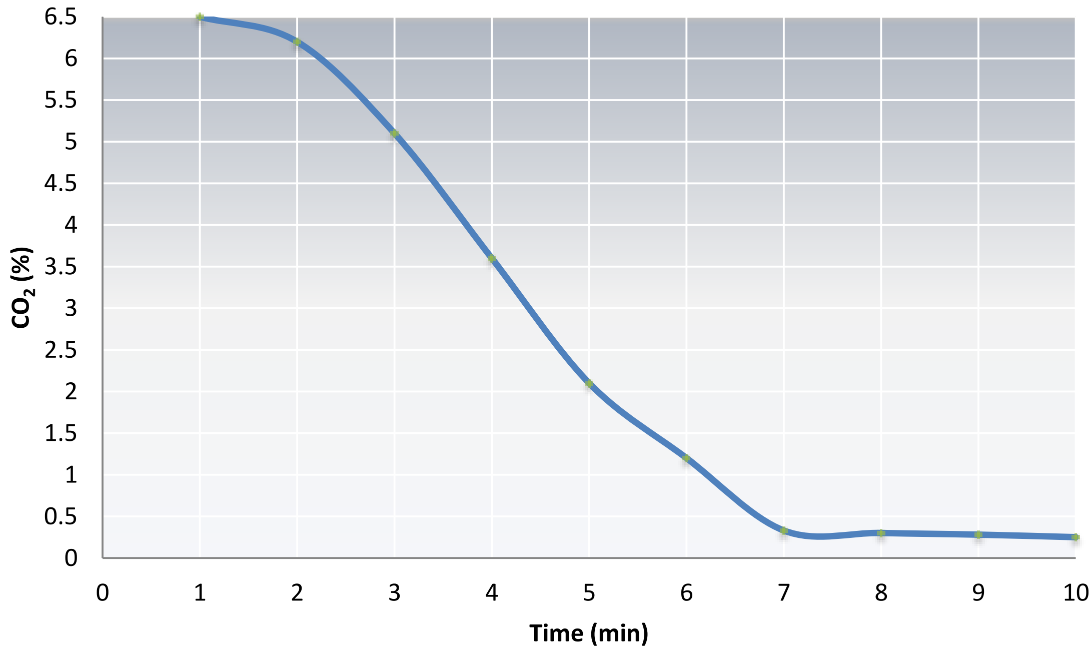
4.1 Scenario A: 30% MEA

4.1.1 CO_2 Absorption

In this scenario, 30% by weight concentration of MEA solution was prepared as solvent. **Figure 4.1** shows initial reading of CO_2 is calculated to be 6.5%. Concentration of CO_2 decreases nearly up to 0.3%, which shows approximately 96.82% removal efficiency.

The conceptual designs of amine scrubbing systems assume 90% CO_2 removal. Seventy to 95% removal represents the range where the cost of CO_2 removal ($/ton) is minimized (Rochelle 2009). In the work by Yeh and Bai (1999), maximum CO_2 removal efficiency and loading capacity by MEA absorbent was calculated to be 94% and 0.40 Kg CO_2/Kg MEA, respectively.

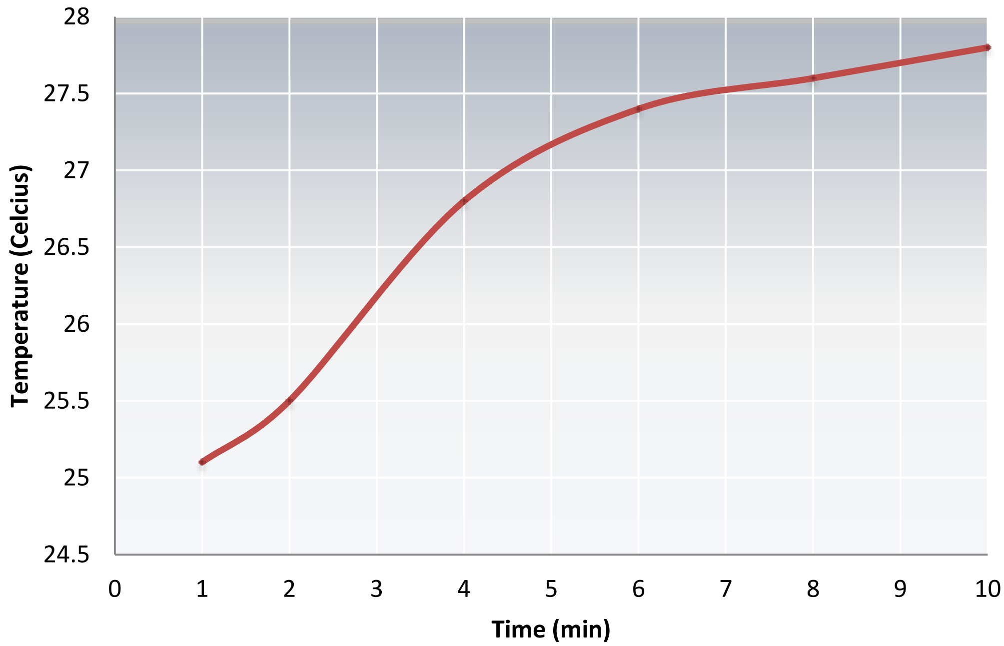
Figure 4.1: CO_2 Absorbed by 30 % MEA



4.1.2 Temperature

As shown in **Figure 4.2**, temperature shows an increase. This increase is due to chemical absorption of flue gases into MEA solvent and the incoming heated gases from motorbike's exhaust.

Figure 4.2: Temperature in Absorber

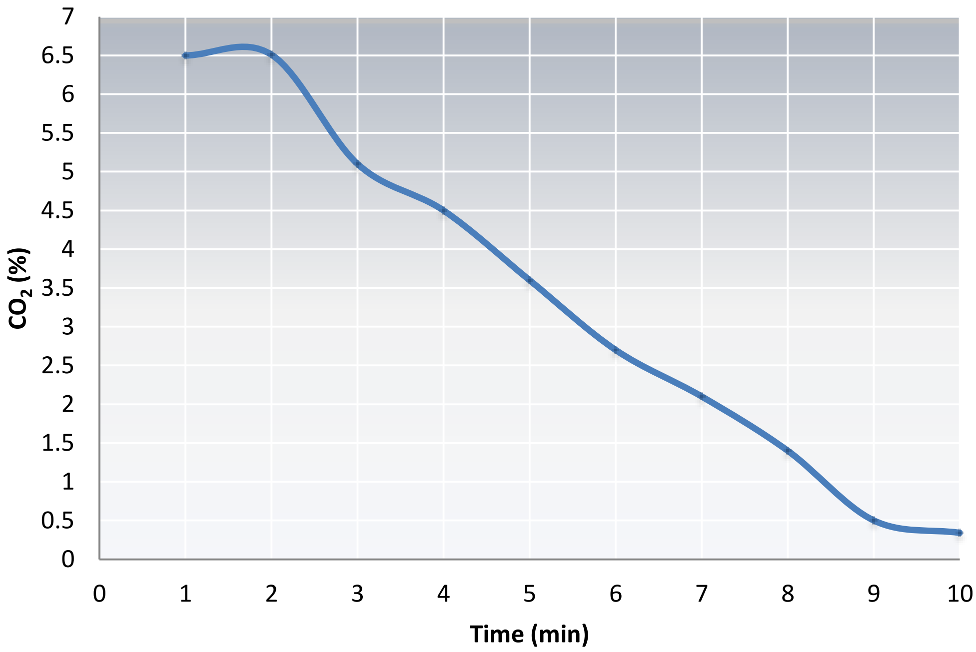


4.2 Scenario B: 20% MEA

4.2.1 CO_2 Absorption

A solution of 20% MEA is showered in the Absorber unit; a decline in the concentration of CO_2 due to this showering takes place. CO_2 concentration decrease from 6.5% to 0.4% achieving 96% removal efficiency. This concentration is not as popular for industrial scale as 30% MEA due to high rate of corrosion and low regeneration rate of CO_2. **Figure 4.3** shows the graph for Scenario B results in Absorber.

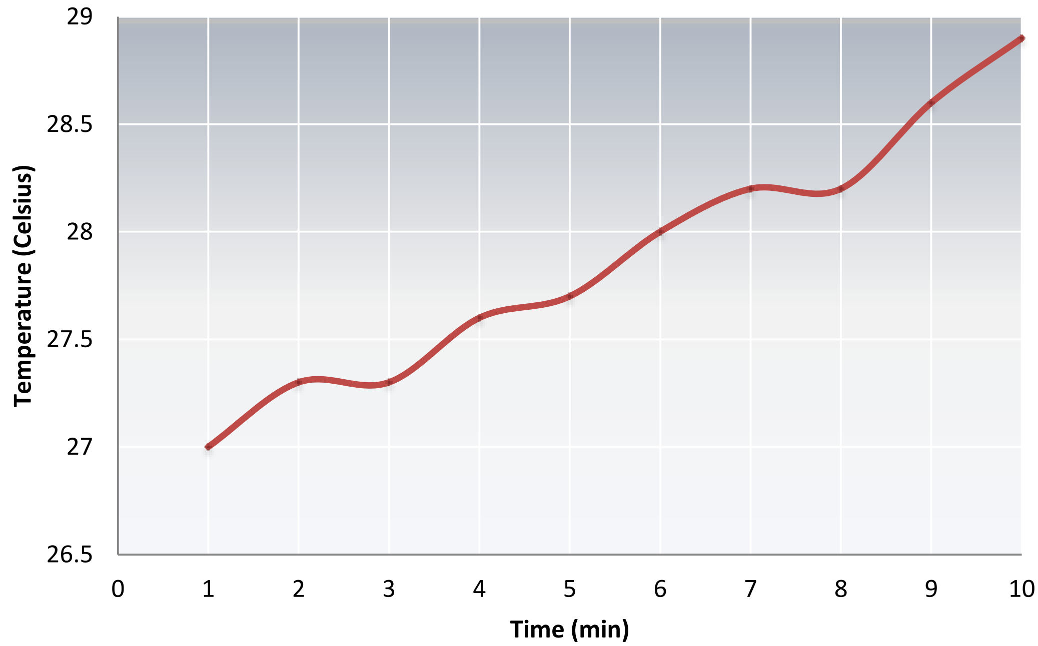
Figure 4.3: CO_2 Absorbed by 20 % MEA



4.2.2 Temperature

According to **Figure 4.4,** absorber temperature increased from 27-29^{o}C. This increase in temperature is due to the high temperature of flue gases entering from exhaust of motorbike to the inlet of absorber unit.

Figure 4.4: Temperature in Absorber

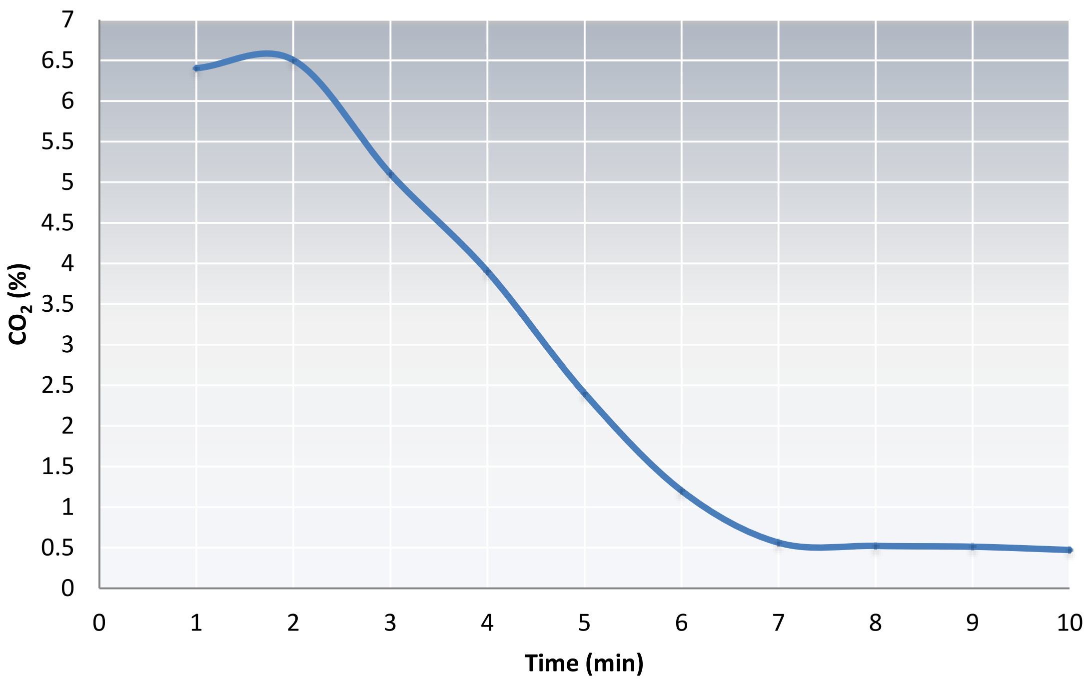


4.3 Scenario C: 30% DEA

4.3.1 CO_2 Absorption

When using a 30% concentration of DEA, a 6% decrease in CO_2 concentration is noted as shown in **Figure 4.5.**

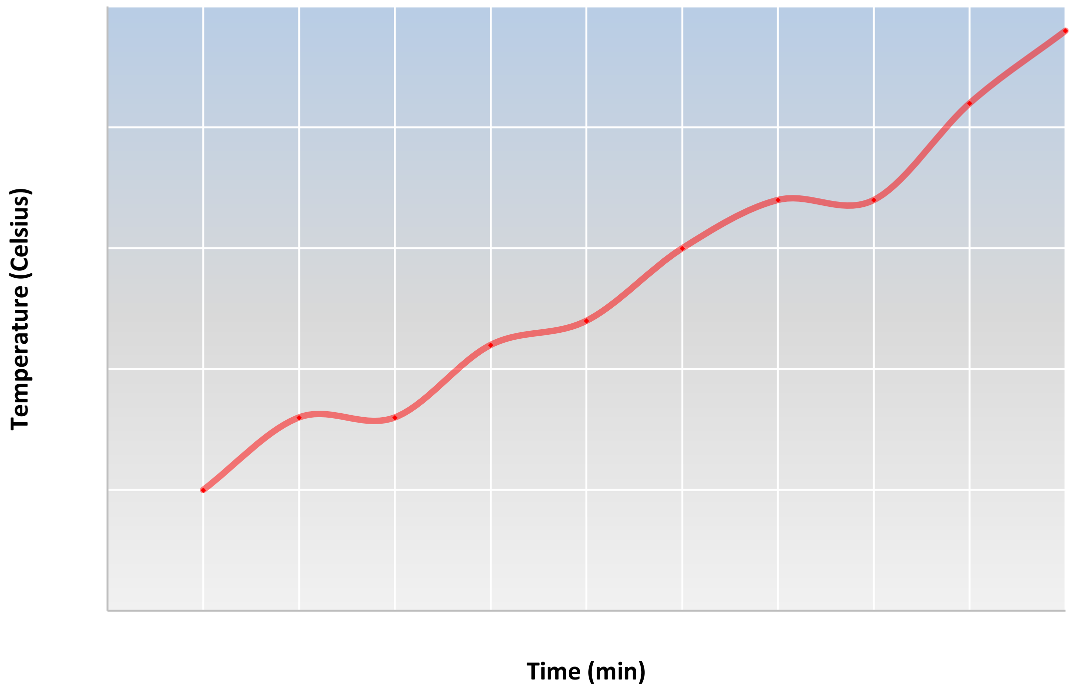
Figure 4.5: CO_2 Absorbed by 20 % MEA



4.3.2 Temperature

Figure 4.6 shows temperature variations when 30 % DEA is added in the absorber unit. A rise in temperature is witnessed. Rise in temperature is due to heated exhaust gases entering the unit and chemical interaction between 30 % DEA and CO_2.

Figure 4.6: Temperature in Absorber

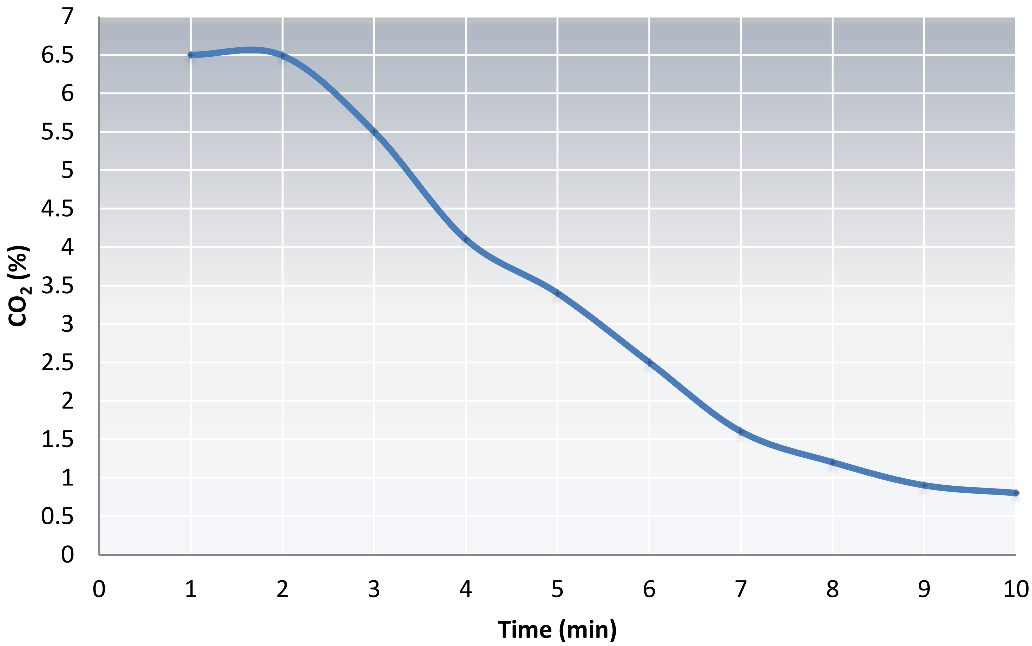


4.4 Scenario D: 20% DEA

4.4.1 CO_2 Absorption

CO_2 concentration level in the absorber unit decreases with the introduction of 20 % DEA as shown in **Figure 4.7**. The efficiency of 20% DEA solution is relatively less than 30 and 20 % MEA solution due to lower degradability of DEA. Efficiency of 20% DEA is calculated to be 87.58%.

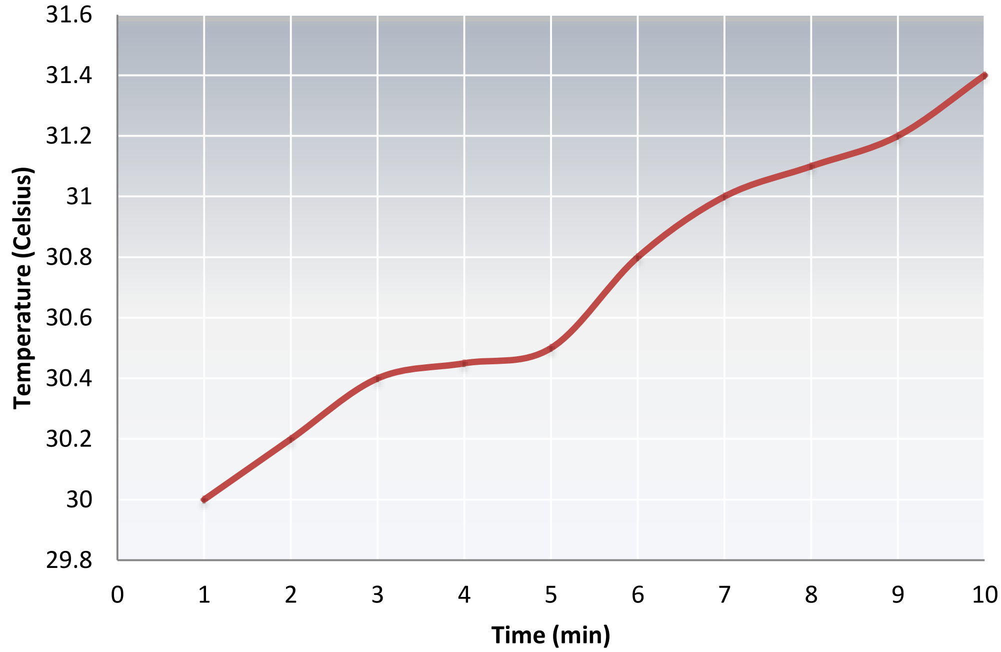
Figure 4.7: CO_2 Absorbed by 20 % DEA



4.4.2 Temperature

Figure 4.8 shows an increase in the temperature of absorber unit which is due to introduction of flue gases from exhaust through inlet of absorber unit. Rise of approximately 1.5 degree is witnessed.

Figure 4.8: Temperature in Absorber



5. CONCLUSIONS

Ever since the industrial revolution following World War II, the world's global Green House Gas Emission has remained the a crucial environmental problem. These unchecked and uncontrolled emissions, that have now become a necessity of the First World, have created huge direct and indirect consequences. Global warming, glacier melting, unexpected floods, heat waves, cold spells and ozone depletion have alarmed nations all over the world. While 50 years ago, environment was nobody' concern, it has now become the primary focus of international and local organizations worldwide.

Greenhouse gases include methane, carbon dioxide, water vapors and other trace gases. Among them, carbon dioxide takes precedence in terms of largest production rates annually. Carbon dioxide is important to life. It plays a role in the most basic life processes. It comes as an unavoidable by-product of industrial development. It is produced by all life forms in the ocean and on land. Currently, the China is releasing 10 billion tons of CO_2 per annum while the United States is second on the list producing 5.9 billion tons annually. Other major CO_2 producers include India, Russia and Japan.

This alarming rate of CO_2 production, resulting in a major disturbance of nature's delicate balance led to drastic measures. The Kyoto Protocol in 1997 established the concept of carbon credits. Over the years following the Kyoto Protocol, many countries have endeavored to cut down on carbon emissions. The United Nations and other international organizations have stressed the importance of using cleaner industrial technologies. Measures such as ISO 14001 certification have been introduced to encourage industries to reduce their carbon emissions.

The position of Pakistan in the context of global environmental polluters is not alarming. However, as unfortunately the country bears a heavy brunt of global warming and climate change resulting due to global industrial activities. In July 2010, Pakistan suffered from the worst flood recorded in history. Since 2000, monsoon trends have been disturbed resulting in heavy flash floods, extreme precipitation and heat waves in different parts of the country. The Siachin Glacier has already receded by about 6 kilometers in the last 2 decades. This situation is a wakeup call.

Over the last decade, China and India have emerged as Asia's economic giants. The overnight industrial progress on Chinese mainland has resulted in huge CO_2 emissions. Pakistan, being a neighbor to both these countries, is suffering the consequences.

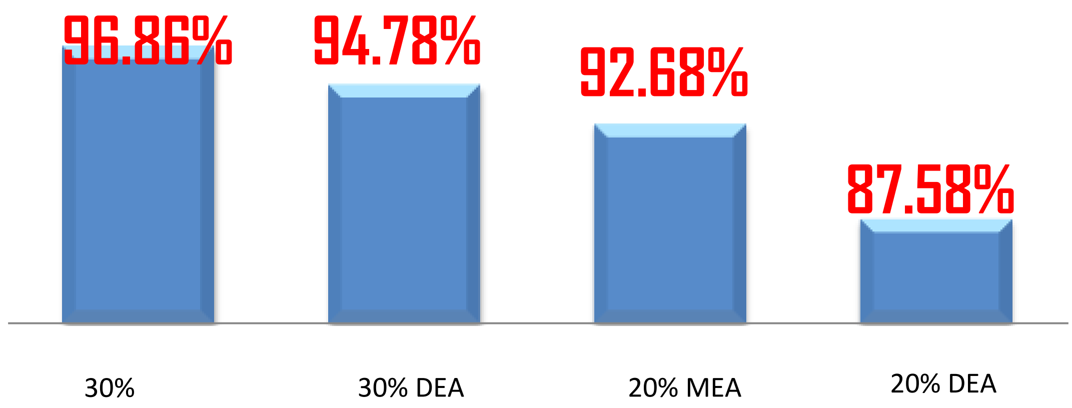
Realizing this problem, the need of the hour is to design and engineer solutions that aim for cleaner industrial production techniques. Sweden, Germany and other European countries are leading the race of innovative CO_2 sequestration technologies. Filter bags, cyclone separators, Emission absorbers and biological techniques are being applied to control CO_2 at the source.

Once such solution to carbon sequestration is presented by this project. Ultra Magnus is a carbon dioxide scrubber designed on a scale of 1:10000, for industrial units. This CO_2 scrubber uses MEA as a solvent to absorb CO_2 from flue gases emitted from industrial units, and release clean gases into the atmosphere.

After many trials & experimentation with the solvent and prototype designs, following conclusions are drawn:

- MEA is an optimum solvent for absorption of CO_2 from flue gases in industrial units. In the prototype tested during the course of this research, MEA yielded an efficiency of 96%. At low temperatures in the absorber unit, efficiency of MEA is even higher. The temperature in absorber unit increases as MEA is showered in the absorber. This increase is probably due to introduction of hot flue gases from source and formation of CO_2 and MEA complex.
- While 30% MEA solution showed highest efficiency, 30% DEA yielded a 94.78% efficiency followed by 20% MEA and 20% DEA solutions. From the data previously mentioned in this research, it is concluded that 30% MEA is the optimum solvent with highest CO_2 absorption efficiencies. MEA is also relatively economical as compared to DEA.

Figure 5.1: Comparison of Efficiencies of Amine Solvents



- At 120°C in the Desorber, CO_2 is separated from MEA and drawn out to be stored. MEA is recycled through the recycle line back to the absorber. Temperature in Desorber unit must be maintained carefully. Temperatures below 120°C will not result in separation of CO_2 from the solvent.
- The design was altered to remove the extra cost and requirement of operating an additional pump for the recycle line. Natural gravitational flow did not result in any design complications.
- DEA at 20% concentration was tested as a solvent and its overall efficiency was calculated to be 87.58 %. This demonstrates that MEA is more efficient but and has additional advantage of cost effectiveness (DEA has higher cost as compared to MEA).
- Corrosion is the major problem with CO_2 scrubbing systems using solvents. After experimentation with different material such as galvanized iron, poly vinyl chloride and thermoplastics, stainless steel was found to be the most suitable corrosion resistant and long lasting material. In order to avoid corrosion caused by production of nascent oxygen in absorber, zinc may be added to the container. Design modifications and chemical solutions to minimize effects of corrosion may be further researched.
- Absorber and Desorber dimensions were standardized after a series of experimentations. Tetrahedral pyramid structures were chosen for final design due to lowest manufacturing costs and most efficient contact time as demonstrated by results achieved. Tests were

conducted with cylindrical and pyramidal units and no loss of efficiency was recorded in the second case.

- Provided time and research resources, Ultra Magnus will endeavor to test the potential of chemically engineered laboratory solvents that may be used for local CO_2 scrubbing technologies.
- Ultra Magnus presents huge potential to local manufacturers and industrialists as a source of boosting production standards, company's public and global image, international environmental certification and reduce cost on energy (provided biofuel technology be coupled with CO_2 scrubbing). Ultra Magnus offers a cheap alternative solution to local industries as a means to reach international standards of processing and production.

6. RECOMMENDATIONS AND FUTURE DIRECTIONS

- The current research work, “Ultra Magnus” has laid the preliminary grounds for research in Carbon sequestration techniques at national scale. While the research objectives aimed to compare different solvents for efficiencies in chemical absorption and design a prototype at minimum cost and minimum energy utilization, considerable effort is still required to meet international standards in carbon requisitioning technologies. As mentioned earlier, CO_2 emissions and resultant climate change will be significant problems addressing future needs. It is the need of the hour to pay serious attention to the issue of global warming due to high CO_2 rates.
- Further ground for technical research in design exists. Cost may be reduced by substituting a stainless steel with another corrosion resistant material. Solvent may be substituted for a higher efficiency solvent.
- In order to supplement this research, the efficiencies of synthetic chemicals as solvents in chemical absorption systems may be tested. Synthetic chemicals will not only provide cheaper solvent replacement options but also improve overall efficiency of scrubbing process.
- Storage of captured CO_2 is another important research point. A possible option is to compress and store CO_2 in underground wells. However, Ultra Magnus proposes to utilize captured CO_2 on algal farms for production of bio fuel. This may mean a possible source of power for the industry and a definite reduction in energy bills. The greatest drawback with CO_2 scrubbers is their huge power consumption factor. This may be substantially reduced if industries opt for bio fuel produced from captured CO_2. Further research on this topic may be conducted as continuation of this research work.
- Power utilization, especially in the Desorber unit, CO_2 compression and storage techniques and cleaning and maintenance are a huge drawback of such systems. Further research in CO_2 storage methods or energy production from the captured CO_2 may result in tremendous profitable opportunities for large and small businesses.

- Expensive design of CO_2 scrubber is another major problem due to its high capital costs. Stainless steel systems are corrosion resistant even at very high solvent concentrations. Possible change of solvent or innovation in corrosion resistant technologies/corrosion preventive chemicals may bring about a revolution in CO_2 sequestration system engineering. In lieu of this research, study on degradation products of amine solvents and how to minimize their adverse effects on the system may be possible areas to be explored for future research.

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Appendix A:

A.1 Experiment Record Form for Ultra Magnus Test Runs

ULTRA MAGNUS EXPERIMENT RECORD FORM

Experiment No: ________________

Recorded by: __________________

Fuel Source: ___________________

Source CO_2 Conc. (%): _________

Ambient Temp (^oC): _____________

Date: ____/_____/201_____

Day: ____________________

Start time: ________________

End Time: ________________

S. No	*Time (hr:min)*	*CO_2 (%)*	*Temperature (^oC)*	*Remarks*
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

Comments:

____

____

Signature: _________________________