

**32nd Annual WERC Environmental Design Contest: Task 5 Controlling VOC
Emissions from Produced Water Recycling**



**Northern Arizona University
Department of Environmental Engineering**

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ABBREVIATIONS

AZ	A dsorption Z one
bb1	B arrel
CAA	C lean A ir A ct
CAPEX	C apital E xpenses
CENE	C ivil and E nvironmental E ngineering
CMC	C ritical M icellar C oncentration
EnE	E nvironmental E ngineering
ENG	E ngineer
EPA	E nvironmental P rotection A gency
ESP	E xperimental S afety P lan
FE	F undamentals of E ngineering
GAC	G ranulated A ctivated C arbon
GCMS	G as C hromatography- M ass S pectrometry
HFCLM	H ollow F iber C ontained L iquid M embrane
IAQ	I ndoor A ir Q uality
INT	E ngineering I ntern
MSW	M unicipal S olid W aste
NAAQS	N ational A mbient A ir Q uality S tandards
NESHAPS	N ational E missions S tandards for H azardous A ir P ollutants
NPDES	N ational P ollutant D ischarge E limination S ystem
NSPS	N ew S ource P erformance S tandard
ORP	O xidation R eduction P otential
OPEX	O perational E xpenses
PDMS	P oly d imethylsiloxane
PE	P rofessional E ngineer
PEBA	P olyether- b lock- a mid
PFD	P rocess F low D igram
P&ID	P iping and I nstrumentation D igram
POMS	P olyoctyl m ethyl S iloxane
PW	P roduced W ater
SENG	S enior E ngineer
SOP	S tandard O perating P rocedure
SPOT	S alinity, p H, O RP, T urbidity
STEM	S cience, T echnology, E ngineering, and M ath
TEA	T echno- E conomic A nalysis
TECH	L ab T echnician
UV-VIS	U ltraviolet- V isible S pectroscopy
VB	V alence B onds
VOCs	V olatile O rganic C ompounds
WERC	W aste- M anagement E ducation and R esearch C onsortium

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1.0 EXECUTIVE SUMMARY

The design problem was introduced by the 32nd Waste-Management Education and Research Consortium (WERC) Design Competition. Specifically, NAU worked on the solution for Task 5: controlling volatile organic compounds (VOC) emissions from produced water recycling. In response to a more stringent regulation on VOCs, NAU was tasked to find a solution to limit VOCs from a 50,000 bbl/day produced water recycling operation to under a 2 ton per year potential to emit limit.

Produced water (PW) is water recovered from hydraulic fracturing and oil recovery and is contaminated with various chemicals such as toluene and other VOCs. The proposed treatment process and the accompanying bench scale model are required to be a closed system, preventing toluene's release to the atmosphere before treatment, and therefore reducing the negative health effects caused by VOC release. The reduction of VOC emissions will curtail low level ozone production which is an issue of concern related to the health of both humans and the environment.

To determine the best treatment options, methods of mass transfer including a spray tower, packed tower, bubble column, sieve tray, and steam stripping were considered. Selecting the best primary treatment method was done by considering cost, the rate of mass transfer, ability to scale up the selected process, treatment time, and how innovative the idea was. Mass transfer calculations ultimately lead to selecting the bubble column, and the choice to treat toluene in its vapor phase. The addition of an adsorption material was necessary to capture toluene vapor after the mass transfer process and prevent its release. A variety of adsorption materials were evaluated using the same criteria as the primary treatment methods before biochar was ultimately incorporated into the bench scale model and full-scale process.

NAU has developed a bubble column reactor with a biochar adsorption column to limit the potential to emit VOCs, specifically toluene, during produced water recycling. Design was performed to scale the bench scale model up to a full-sized treatment process that treats produced water at the rate of 50,000 bbl/day while reducing the potential to emit to under 2 tons per year

of VOCs. Installation of this full-scale design will cost \$783,850 and total operating costs come out to \$0.16 per barrel (bbl) of produced water or \$2,920,000 per year. The construction process and community outreach will last 1-2 years.

This design provides effective treatment for reducing the concentration of toluene in produced water to under 2 ppm and accumulates to less than 2 tons/year in a full-scale setting for a minimal additional treatment cost.

2.0 PROJECT INTRODUCTION

2.1 PROJECT PURPOSE

The purpose of this project is to design a treatment method and create a bench-scale model to remove VOCs from oil and gas PW and provide clean, recycled water for reuse without releasing the VOCs into the atmosphere prior to treatment.

2.2 PROJECT BACKGROUND

Demonstration of the bench-scale model constructed by the team will be performed and used to test the treatment process's ability to remove VOCs. The final intention of the model is for its treatment process to be scaled up for use in a full-scale facility that can handle 50,000 bbl/day as a closed system. For the purposes of this project, VOCs will be represented by the presence of toluene. At the competition, testing for the presence of toluene in the treated water will be done using either Liquid Chromatography with Ultraviolet-visible spectroscopy (UV-VIS) detection for toluene or gas chromatography (GC). The team will use a GC during the design and testing process because it is available in NAU's environmental engineering lab. To abide by state laws, VOCs in the PW recycling industry are expected to be limited to 2 tons per year based on the potential to emit.

VOCs are a common pollutant found in by-product water from oil and gas operations. There are currently PW recycling processes in place, but US states are proposing to limit VOC levels in PW recycling based on the potential to emit, which does not consider the actual VOCs emitted into the atmosphere but only what is present in the aqueous phase. VOC levels in raw produced water can be anywhere from >10 ppm to >100 ppm. The PW solution to be tested is a synthetic sample of produced water based on water characteristics of PW from the Delaware shale play. The Delaware Basin, shown in Figure 2-1, where the shale play resides is a basin known for its large oil fields and is in West Texas and southern New Mexico [1]. The most prominent PW practices involve the storage and recycling of PW for reuse in hydrofracturing.

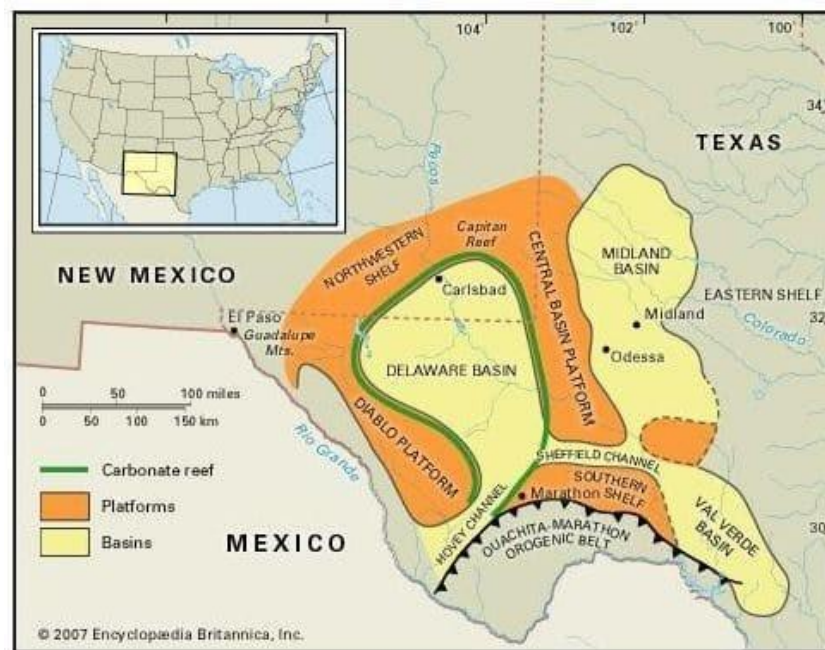


FIGURE 2-1: DELAWARE BASIN SITE MAP

2.3 CONSTRAINTS AND LIMITATIONS

This project has the potential to encounter several problems. One of the potential issues is the progression of the COVID-19 pandemic during this project. If the spread of COVID-19 increases, it could hinder lab access, decrease the quality of communication, and cancel the

in-person aspect of the WERC competition altogether. This challenge is out of the team's control, but measures can be taken to prepare for different end scenarios.

Another potential challenge is the budget for the fabrication of the bench-scale model. Limited funding is available for materials and equipment, so the design of the bench-scale model will need to take this into account. If funding for the project becomes an issue, there is the possibility of fundraising to increase the budget. Furthermore, the size of the bench-scale model is a limiting factor as well since the team intends to transport the model to New Mexico without involving a 3rd party.

Availability of testing equipment is another potential challenge. The environmental lab at Northern Arizona University may not have all the testing equipment needed to determine parameters requested by the competition, so the equipment might need to be acquired or another lab utilized for certain tests.

All these potential challenges were considered beforehand so that when they were encountered in the project, their impacts were minimized.

3.0 BACKGROUND RESEARCH

3.1 ANALYSIS OF TREATMENT ALTERNATIVES

The analysis of treatment options was conducted in three steps including background research, stripping alternatives, and weighted decision matrices. Two different types of treatment options were considered: liquid adsorption and gas adsorption after a stripping technology is used to vaporize the aqueous toluene from the PW. The adsorption materials were considered together for both liquid and gas applications, and the stripping alternatives were considered separately.

3.1.1 STRIPPING BACKGROUND RESEARCH

E-Z Tray Air Stripper - An E-Z Tray Air Stripper, patented technology, is “a sliding tray, stainless steel air stripper ideal for removing volatile organic compounds (VOCs) from contaminated groundwater and waste streams” [2]. This technology can also be adapted to create an alternative to traditional air stripping. Stripping ultimately works by causing the contaminated water to contact air with a very large surface area. This provides diffusion through a concentration gradient within the VOC free air bubbles as the VOC’s seek to reach equilibrium between the air and water. This mass transfer can be performed through various equipment including a countercurrent packed tower or a bubble column. The bubble column works by forcing air bubbles through the contaminated water to cause mass transfer from the VOCs in the contaminated water to the high surface area bubbles. The VOCs are then treated in the air using another technology to minimize emissions.

Steam Stripping - Steam stripping is an alternative to traditional air stripping. This technology would also allow the VOCs to become concentrated as a liquid for possible repurposing. The process works by “reducing the partial pressure of the pollution by heating and creating a positive mass transport from the water to the gas phase via steam injection” [3].

Packed Tower – Packed towers are described as vertical columns that are filled with various packing materials. This technique is also to provide continuous contact of the gas and liquid phases making it effective at removing contaminants. Packed towers are also able to provide a large contact area for mass transfer [4]. A packed tower can be used when either phase, gas, or liquid, controls the rate of mass transfer [4]. Packing materials can include numerous sized rings or saddles as shown in Figure 3-1.

Table 30.2 Packing coefficients for equation (30-37)

Packing	α	n
2.0 inch rings	80	0.22
1.5 inch rings	90	0.22
1.0 inch rings	100	0.22
0.5 inch rings	280	0.35
0.375 inch rings	550	0.46
1.5 inch saddles	160	0.28
1.0 inch saddles	170	0.28
0.375 inch saddles	150	0.28
3.0 inch spiral tiles	110	0.28

FIGURE 3-1: PACKED TOWER PACKING COEFFICIENTS [4]

Bubble Column – A bubble column is used as an alternative utilizing the concept of air stripping. Bubble columns operate by bubbling “air into the bottom of a vessel containing liquid water” [4]. This is a form of gas-liquid mass transfer for the contaminants present in the liquid water. There are two types of bubble column reactors. First, traditionally, “gas is sparged into the bottom of a tube” [4]. This is typical of aerobic technology in wastewater treatment. The second technology is where “gas is sparged into a tank filled with liquid that is mixed with a rotating, submerged impeller” [4]. This method can provide continuous contact, unlike the traditional method but is often more expensive because of the need for impeller installation and maintenance.

Bubble columns are effective at removing VOCs from water. This is because the formation of fine bubbles provides a large contact area for mass transfer [4]. In addition, bubble columns are also effective for processes that are liquid phase controlled [4].

Spray Tower – A spray tower is described as a stripping technology where “the gas phase flows up through a large open chamber and the liquid phase is introduced by spray nozzles or other atomizing devices” [4]. This produces many small droplets giving the interphase contact area for mass transfer. However, with the use of small droplets and a nozzle, the technology runs a risk of producing entraining, superfine

droplets which could be hazardous. Spray towers are also most effective when used on soluble compounds where the gas-phase controls the rate of mass transfer [4].

3.1.2 BUBBLE COLUMN CALCULATIONS

The mass transfer capacity coefficient was calculated for the bubble column and describes the efficiency of mass transfer. The temperature was 20°C and pressure was determined to be 0.8 atm in the lab since it is located at elevation in Flagstaff. A table of the constants used for the stripping calculations is shown in Appendix C.

The first step in determining the mass transfer coefficient for the bubble column was to determine the size of the bubbles. This can be calculated based on the pore size of the bubbler, which in this case is a 2-micron diffusion stone. Equation 3-1 below shows how to calculate the bubble diameter [4]. This is used to calculate the area available for mass transfer. Smaller bubble diameters are optimal.

EQUATION 3-1: BUBBLE DIAMETER

$$d_b = \left(\frac{6d_o\sigma_L}{g(\rho_L - \rho_G)} \right)^{1/3} \quad (1)$$

- d_b = bubble diameter
- d_o = bubbler pore diameter
- σ_L = water surface tension
- g = gravitational acceleration
- ρ_L = water density
- ρ_G = air density

The bubble diameter can then be used to calculate the Grashof number which is shown as Equation 3-2 below [4]. This is used to calculate the relationship between buoyancy and viscosity and proves if mass transfer is viable.

EQUATION 3-2: GRASHOF NUMBER

$$Gr = \frac{d_b^3 \rho_L g (\rho_L - \rho_G)}{\mu_L^2} \quad (2)$$

- d_b = bubble diameter
- g = gravitational acceleration
- ρ_L = water density
- ρ_G = air density
- μ_L = water liquid viscosity

The next calculation needed for the determination of the mass transfer coefficient is the Schmidt number shown in Equation 3-3 below [4]. This number is used to show the fluid flow feasibility.

EQUATION 3-3: SCHMIDT NUMBER

$$Sc = \frac{\nu}{D_{AB}} \quad (3)$$

- Sc = Schmidt number
- ν = water kinematic viscosity
- D_{AB} = liquid phase diffusivity constant

The last value that needs to be found before the mass transfer coefficient can be calculated is the Sherwood number, using Equation 3-4. This equation is only valid for bubble diameters less than 2.5 mm [4]. This is used to show a relationship between mass transfer and mass transport.

EQUATION 3-4: SHERWOOD NUMBER

$$Sh = 0.31 Gr^{1/3} Sc^{1/3} \quad (4)$$

- Sh = Sherwood number
- Gr = Grashof number
- Sc = Schmidt number

Finally, using the Sherwood number, the mass transfer coefficient can be calculated. Equation 3-5 below shows the calculation of the mass transfer coefficient [4].

EQUATION 3-5: MASS TRANSFER COEFFICIENT

$$k_L = \frac{Sh \times D_{AB}}{d_b} \quad (5)$$

- k_L = mass transfer coefficient
- Sh = Sherwood number
- D_{AB} = liquid phase diffusivity constant
- d_b = bubble diameter

Unlike the bubble column, for the packed tower it is difficult to determine the interfacial mass transfer area available, and the mass transfer coefficient is presented as a capacity coefficient kLa . To compare the two stripping technologies, therefore, the bubble column mass transfer coefficient must be converted to a capacity coefficient. This is done by determining the total volume of bubbles in the water during treatment and calculating the gas holdup ratio, using Equation 3-6. The volume of gas bubbles within the water is determined experimentally, but since the column was not constructed prior to these calculations the gas volume had to be estimated based on a lab bubbling test in a large, graduated cylinder.

EQUATION 3-6: GAS HOLDUP RATIO

$$\Phi_g = \frac{V_g}{V} \quad (6)$$

- Φ_g = gas holdup ratio
- V_g = volume of gas bubbles within the water
- V = volume of water

The interphase mass transfer area available per unit volume, a , can then be calculated with Equation 3-7.

EQUATION 3-7: INTERPHASE MASS TRANSFER AREA PER UNIT VOLUME

$$a = \frac{6\Phi_g}{d_b} \quad (7)$$

- a = interphase mass transfer area per unit volume
- Φ_g = gas holdup ratio
- d_b = bubble diameter

Finally, the capacity coefficient for the bubble column is calculated by multiplying the mass transfer coefficient k_L by the interphase mass transfer area per unit volume, a. This is shown in Equation 3-8. This is used to determine the rate of mass transfer.

EQUATION 3-8: MASS TRANSFER CAPACITY COEFFICIENT

$$k_L a = k_L * a \quad (8)$$

- a = interphase mass transfer area per unit volume
- k_L = mass transfer coefficient

Table 3-1 summarizes all the calculations for the bubble column and shows the final calculated values.

TABLE 3-1: BUBBLE COLUMN CALCULATIONS

Bubble diameter, d_b	0.000447	m
Grashof number, Gr	904.69	unitless
Schmidt number, Sc	1223.86	unitless
Sherwood number, Sh	32.07	unitless
Mass transfer coefficient, k_L	0.0000583	m/s
Gas volume in column, V_g	0.0000326	m ³
Liquid volume in column, V	0.0005	m ³
Gas holdup ratio, ϕ_g	0.065	unitless
$a = A_i/V$	874.34	m ² /m ³
$k_L a$	0.0510	1/s

The result of this calculation shows a mass transfer rate of 0.05 1/s. This is indicative of a high rate of mass transfer. This number proves that mass transfer in the bubble column occurs at a rate sufficient to use in a final design.

3.1.3 PACKED TOWER CALCUALTIONS

The capacity coefficient $k_L a$ for the packed tower required a different calculation process. The calculation of $k_L a$ is dependent on the packing materials within the column as well as the liquid flow rate. As seen in equation 3-9 below, a higher liquid flow rate will yield a higher capacity coefficient. The highest reasonable liquid flow rate that a bench scale sized packed tower could handle was used to calculate the capacity coefficients to give the highest values that could be achieved by a bench scale system.

EQUATION 3-9: PACKED TOWER CAPACITY COEFFICIENT

$$k_L a = D_{AB} \alpha \left(\frac{L}{\mu_L} \right)^{1-n} \left(\frac{\mu_L}{\rho_L D_{AB}} \right)^{0.5}$$

- $k_L a$ = capacity coefficient
- D_{AB} = liquid phase diffusivity constant
- α = packing coefficient
- L = liquid mass flow rate per cross sectional area of the tower
- μ_L = water liquid viscosity
- n = packing coefficient
- ρ_L = water density

The packing coefficient values for α and n and values for all constants can be found in Appendix C. Table 3-2 below shows a summary of calculations for the packed tower based on the different packing type within the column.

TABLE 3-2: PACKED TOWER CAPACITY COEFFICIENTS

Packing Type	$k_L a$ (1/s)	Liquid Flow Rate (gpm)
2.0-inch rings	0.00273	0.3963
1.5-inch rings	0.00307	0.3963
1.0-inch rings	0.00341	0.3963
0.5-inch rings	0.00435	0.3963
0.375-inch rings	0.00439	0.3963
1.5-inch saddles	0.00380	0.3963
1.0-inch saddles	0.00403	0.3963
0.375-inch saddles	0.00356	0.3963
3.0-inch spiral tiles	0.00261	0.3963

As seen in the table, the 0.375-inch rings provide the highest mass transfer capacity coefficient of 0.0044 L/s, but when comparing the value to the capacity coefficient for the bubble column, the value is significantly smaller. These capacity coefficient calculations are reflected in the rate of mass transfer category of the decision matrix in the next section and significantly contributed to the selection of a final treatment design.

3.1.4 LIQUID AND GAS ABSORPTION BACKGROUND RESEARCH

Nanophotocatalytic Degradation - This process requires synthesis of nanoparticle maghemite [5]. The process is described as “Nanophotocatalytic semiconductors have two energy levels in their structure valence bands (VB) and, conduction band VB. When the semi-conductors exposed to the photons which, energy is equal to or greater than the band gap energy, the electrons (e^-) in the VB have been excited” [5]. However, this is a very precise method because pH and light intensity need to be considered in the design.

Microfiltration - This technology eliminates the need to utilize air stripping in any form as it will treat VOCs in the water stream. The basis of this technology is that “at concentrations above the critical micellar concentration (CMC), surfactant

molecules attach to each other forming organized aggregates or micelles” [6]. This is also a form of in-situ treatment. During research, this technology was overall found to be effective at removing VOCs.

Pervaporation (PDMS/POMS) - An additional alternative considered was pervaporation with a polydimethylsiloxane (PDMS) or polyoxymethylene siloxane (POMS) membrane. Pervaporation is conducted by a method where “the aqueous solution passes through one side of a polymeric membrane highly selective toward the organic solutes and vacuum is applied on the other side” [7]. This technology is like reverse osmosis, but the driving force is a vacuum on one side of the membrane which causes a phase change [7]. The membrane of choice will be placed on the vacuum side where “the organic solutes, along with some water, dissolve and diffuse through the polymeric membrane and subsequently condensed and separate” [7].

Pervaporation (PEBA) - Another alternative of pervaporation was researched using polyether-block-amide (PEBA) membranes. This method produced ~80% removal in a 5-hour experiment. The same pervaporation method will be used, but with a different type of membrane. The removal of toluene using this membrane was like the removal process described for PDMS and POMS membranes [8].

Pervaporation (HFCLM) - Again, using the same pervaporation technique, a Hollow Fiber Contained Liquid Membrane (HFCLM) was considered. In this system, “one set of hydrophobic hollow fibers into which the aqueous stream is fed is packed in a shell-and-tube heat exchanger arrangement along with a second set of nonporous hollow fibers in the bores of which vacuum is applied” [9].

Adsorption w/ Municipal Solid Waste (MSW) Biochar - This technology can be used directly in the water or after stripping. It also reduces the overall harmful volume of municipal solid wastes by utilizing it to create biochar. According to the research “biochar is a surrogate for activated carbon and is produced by the slow

pyrolysis of biomass at low temperature” [10]. This will be another potential source of activated carbon, like the coconut activated carbon.

Ionic Liquid Adsorption – This method removes toluene when in its gaseous phase, so again, air stripping or an alternative will be needed before use. The study used an “imidazolium-based ionic liquid as the absorbent solution and combined with a tubular ceramic membrane for the absorption of VOCs from a gas stream” [11]. This filtration method is like the POMS and PDMS membranes. Except in this case, the toluene will be sorbed to the filter and ionic liquids have favorable qualities that favor the adsorption of toluene.

Adsorption w/ Pyrolyzed Peat & Sawdust - This is an in-situ approach and does not require air stripping prior to use. The VOCs are treated by sorption to the pyrolyzed peat or sawdust, then the material is disposed of. According to the research “Biosorption offers an alternative removal technique, and the use of natural materials as well as industrial or agricultural byproducts has shown promising result” [12]. This will most likely be conducted by the group in batch absorption processes.

Adsorption w/ Carbon Nanotubes - This process will be in-situ allowing the team to treat VOCs without an air stripper. This technology works by the “adsorption mechanism of toluene on carbon nano tubes is mainly attributed to the π - π electron donor-acceptor interaction between the aromatic ring of toluene and the surface carboxylic groups of carbon nano tubes” [13].

Adsorption w/ Activated Carbon from Coconuts - This alternative uses a sustainable form of activated carbon to treat the VOCs in the air phase. The primary focus of this technology was to source the activated carbon from coconuts. This plays a dual role in both treating the VOCs and reducing waste from coconut waste. Coconut shell sourced activated carbon was particularly attractive because of the

larger pore size, “activated carbon made from coconut shell is ideal for water filtration, as its tiny micropores match the size of most water-based contaminants” [14].

Adsorption w/ Ground Tires - An adsorption method using ground discarded tires was considered as another more sustainable solution as a replacement for traditional activated carbon. This method is in-situ and removes the VOCs directly from the water. This method works because “the carbon black used to strengthen the rubber, is similar to activated carbon, a good sorbent to remove dissolved organic substances from waste-water” [15].

Adsorption w/ Chitin & Chitosan - These materials are obtained from the shells of crabs. This process works because “Chitosan plays an important role as a complexing agent, because of its high content of hydroxyl and amino functional groups; hence, it has a high adsorption potential to a wide range of contaminants, such as organic compounds” [16].

Adsorption w/ Moringa Oleifera Pods - These pods are a “multipurpose medium or small size tree from sub-Himalayan regions of north-west India and indigenous to many parts of Asia, Africa, South America, and in the Pacific and Caribbean Islands” [17]. This process works similarly to the other absorption processes. It stands out because the pods “have greater surface area and pore diameter, may be due to the fact that chemical treatment can dissolve the minerals and functional groups from the sorbent surface and thus enhances the pore volume” [17].

3.1.5 BACKGROUND RESEARCH SUMMARY

The research covered some atypical alternatives used primarily to inspire potential design options. Nanophotocatalytic degradation, microfiltration, and pervaporation were all eliminated due to varying levels of complexity in implementing the concepts in a bench-scale model. General methods of mass transfer including spray

towers, bubble columns, sieve trays, and packed towers were considered further as the main methods of VOC treatment. Steam stripping also remained a possibility due to its similarities to traditional air stripping. However, all sorption/adsorption methods researched remained viable options except for ionic liquid adsorption which was one of least feasible of the listed options.

Methods of stripping mass transfer including spray towers, bubble columns, sieve trays, packed towers, and steam stripping were considered as methods of VOC treatment.

3.2 DECISION MATRICES

Two decision matrices were created, one for primary treatment methods and another for adsorption materials. These matrices can be seen in Tables 3-1 and 3-2 below.

After the research for potential treatment options, all the treatment options were placed into a spreadsheet. The team analyzed and individually scored each treatment method based on cost, feasibility, rate of mass transfer, innovativeness, and treatment time. Each category was assigned a weight according to what was deemed most important. Rate of mass transfer was assigned one of the largest weights due to project being an actual mass transfer problem and as such it is important that whatever method is chosen removes toluene from the produced water effectively. Innovation shared an equally heavy weight because the competition and team both placed emphasis on working to create a model that incorporated more sustainable and less common ideas. Cost and feasibility were assigned weights of 20% as being able to purchase the materials and determining if certain concepts could be constructed in a model form were limiting what the team could create. Lastly, treatment time was assigned a weight of 10%. This is because the treatment time should not take more than several hours due to limitations set by WERC. Additionally, the team wanted a treatment time that could allow for additional batches of produced water to be run within the given period, so it became a key factor when deciding on a final design. The weighted scores are shown in Tables 3-3 and 3-4 below.

The cost considered was the estimated cost for the implementation at a full-scale treatment plant. Feasibility was how likely the team would be to be able to build a model of the treatment for the competition. Feasibility was influenced by mass transfer coefficient calculations. Steam stripping, sieve tray, and spray tower were unable to be calculated due to the properties of toluene. However, the rate of mass transfer coefficients were calculated for the packed tower and bubble column as shown in section 3.1.2 and 3.1.3. Multiple iterations of the calculation were performed for the packed tower to assess the various options for packing material.

The innovation level was scored based on the creativity and renewability of the treatment method. The treatment time, a contest requirement, was scored on how likely the treatment method would be able to effectively remove VOCs in a short time.

The research gathered is a culmination of both adsorption materials and treatment technology alternatives. Adsorption/sorption materials were often highly integrated within VOC treatment methods researched. However, these materials still exist separately from these different technologies and as such should be considered individually based on their abilities to adsorb VOCs like toluene. Therefore, two decision matrices were created, one for adsorption materials and another for primary treatment methods which were then used to narrow in on a final design. Each team member scored the treatment options independently, and the average of the team's individual scores is what's shown below.

TABLE 3-3: DECISION MATRIX-PRIMARY TREATMENT METHODS

Primary Treatment Methods	Cost (20%)	Feasibility (20%)	Rate of Mass Transfer (25%)	Innovation (25%)	Treatment Time (10%)	Weighted Total
Spray Tower	7	0	8	6	8	6
Steam Stripping	6	0	8	6	6	5
Sieve Tray	9	0	4	7	6	5
Packed Tower	7	8	7	5	8	7
Bubble Column	7	7	8	8	8	8

TABLE 3-4: DECISION MATRIX-ADSORPTION & SORPTION MATERIALS

Adsorption Materials	Cost (20%)	Feasibility (20%)	Rate of Mass Transfer (25%)	Innovation (25%)	Treatment Time (10%)	Weighted Total
Coconut Activated Carbon	5	9	7	6	7	7
Pyrolyzed Peat & Sawdust	6	8	6	6	7	7
Carbon Nanotubes	3	7	8	7	7	7
Ground Tires	7	5	7	8	7	7
Chitin & Chitosan	6	9	3	7	4	6
Moringa Oleifera	7	7	6	8	6	7
Biochar	7	8	7	8	6	8

When determining a final design, the primary treatment method was selected first, followed by two adsorption materials to use in conjunction with the selected process. It is important to note that liquid adsorption was initially considered as well, but based on the properties of the PW, namely the oil, sediment, and clay particles within the water, the team did not expect a liquid adsorption method to perform well and would clog up quickly. This would result in a higher use of adsorption materials causing higher operating costs, more waste, and less sustainability. More than one adsorption material was selected for testing to determine which material would hold the most toluene and provide the highest efficiency removal.

The first consideration when eliminating primary treatment methods from the final design was the feasibility. Feasibility was described as the ability to use the stripping technique for practical use. This included consideration of the availability of materials and properties of toluene that could make the method unusable. The spray tower, steam stripping, and sieve tray were scored a zero for feasibility. The spray tower could not be implemented due to toluene’s relative insolubility. Steam stripping was not possible because of the risk of fine particles. Finally, the sieve tray was not feasible due to a lack of continuous contact time.

The next category used to narrow down the primary treatment methods was the rate of mass transfer. Calculations were performed to determine mass transfer coefficients for the packed tower and bubble column as discussed above. The k_{LA} or mass transfer capacity coefficient was determined to be higher in the bubble column which is indicative of a greater rate of mass transfer. The results indicate that the bubble column had a higher mass transfer coefficient of 0.0510 1/s compared to the maximum packed tower mass transfer coefficient of 0.0044 1/s.

Finally, between the bubble column and steam stripping, the bubble column scored higher in innovation. This occurred for two reasons, 1) the ability to integrate more interesting adsorption materials and 2) because the column is the least like typical air stripping which has already been used and tested a multitude of times in several industries.

Deciding which adsorption materials to use began with considering which products would be more feasible for the vapor phase removal of toluene. Ground tires were eliminated with the lowest feasibility score as it would be most useful when adsorbing aqueous toluene due to the properties of the rubber.

Next, cost and rate of mass transfer became the most effective ways to eliminate more materials. Carbon nanotubes were found to be the most expensive and the allotted project budget would not allow for the purchase of a large quantity of these materials. Moringa Oleifera, chitin and chitosan, and carbon made from peat and sawdust were found to come primarily in powder forms which do not work as well as a granular form for flowing gas streams. Considering this, all three of those options were eliminated. Ultimately, this left MSW biochar and activated carbon from coconuts as the two selected adsorption materials to be purchased and further tested before being used in a gas adsorption column along the bubble column.

4.0 BENCH-SCALE MODEL FABRICATION

4.1 FABRICATION

Fabrication of the model began at the beginning of February after the team had settled on a design and created the process flow diagram. Using the PFD as well as materials sourced in the laboratory, the team started to make construction plans which involved modifications of a repurposed column from the NAU environmental engineering lab. Two holes were drilled in the column for fittings that would allow PW to flow into the column and diffusion air carrying vaporized toluene out of the column. These modifications to the column were carried out by the on-campus CEFNS Research and Machine Shop.

Additionally, the repurposed column already had two sealed acrylic boxes mounted on either end. One of the end boxes had a sealed piping inlet already installed so the team decided that that end would be the top so that the port could be reused. This inlet was ultimately used as a gas sampling port. The box mounted on the other end of the column was removed to allow for the addition of a 2-inch diameter ball valve that would act as the exit for the treated PW. To make this ball valve fit to the end of the column, the team had to use 2-inch diameter PVC piping to close the 1/8th inch gap in between the acrylic column and the ball valve.

Once the major modifications to the column were finished, the team decided to design and build a wooden stand for the column so that the column could be suspended above the treated PW catchment. A photo of the final design is shown in Figure 4-1. AutoCAD representations of the model's final design can be found in Appendix D.

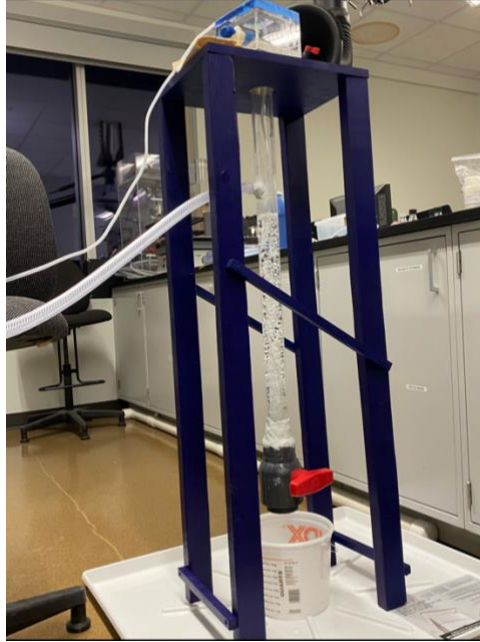


FIGURE 4-1: FINAL BENCH-SCALE DESIGN

5.0 SOLUTION DESCRIPTION

The model design was completed in three parts: the process flow diagram, process design, and drawing production.

5.1 PROCESS FLOW DIAGRAM

A process flow diagram of the proposed solution was created to give a general idea of the steps needed to achieve VOC removal. The process flow diagram in Figure 5-1 shows a visual representation of the overall treatment process design. The process consists of two main treatment components: a bubble column and a gas adsorption column.

Produced water was mixed with a concentration of 50 mg toluene/L of water and stored in a closed bucket. Approximately 70 cubic inches of produced water is transferred into the bubble column, which serves as a batch reactor. This is done using the static fill model. After the produced water is added, the aquarium sized air pump is turned on. This pump is connected to a diffusion stone which produces bubbles at the bottom of the bubble column.

As the bubbles travel up the column of PW, the interphase concentration gradient induces mass transfer of the VOCs into the air stream as VOC vapors. At this point, the air will pass through an adsorption filter and be released into the atmosphere. Figure 5-1 below shows the process flow diagram (PFD) for the treatment process.

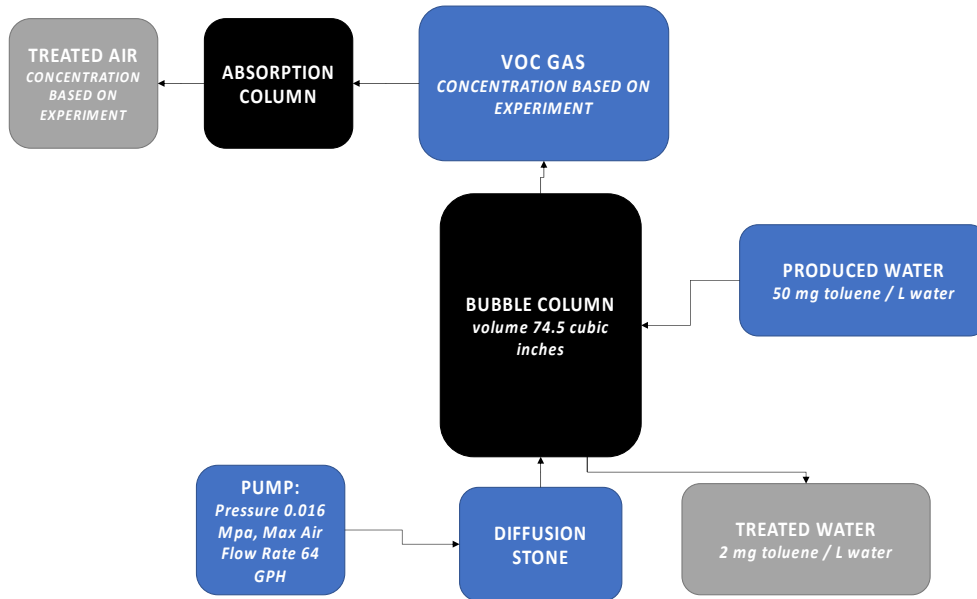


FIGURE 5-1: TREATMENT PROCESS FLOW DIAGRAM

5.2 BUBBLE COLUMN PROCESS DESIGN

The first design consideration concerned the bubble column. The most important concepts to consider when designing a bubble column are the column diameter, fluid height, bubble size, bubble flow regime, gas flow velocity, and mass transfer rate.

The height to diameter ratio of a bubble column should not exceed 12 because the gas to liquid interfacial area decreases through bubble coalescence [18]. The team decided to repurpose an acrylic column with an internal diameter of 1.75 inches and a total height of 36 inches. The maximum water height was selected to be 21 inches, giving a maximum height to diameter ratio of 12.

The desired bubble size for this project is less than 1 mm in diameter which is considered ultrafine [18]. This is because smaller bubble sizes have a lower rising velocity and more contact time with the contaminated water for mass transfer. Smaller bubble diameters and a larger number of bubbles also provide more gas-liquid interfacial area for mass transfer. To incorporate this into the bench scale model, a diffusion stone with 2-micron ultrafine pores was selected. The approximate bubble diameter was then calculated and found to be 0.447 mm.

Next, the bubble flow regime of the system was considered. The flow of bubbles within a bubble column is either homogenous or heterogeneous [18]. Homogenous flow consists of uniform bubbles while heterogeneous flow has varying bubble sizes. The desired flow regime is homogenous flow to avoid bubble coalescence, which decreases the area available for mass transfer and produces faster moving bubbles decreasing contact time. Obtaining homogeneous bubble flow can be done by changing the gas flow rate.

Using Figure 5-2 below and the column diameter of 0.044 m (1.75 inches), the flow velocity of the air was determined. To remain in homogenous flow, the air velocity needs to remain below 0.035 m/s. The maximum volumetric flow rate that the aquarium air pumps can provide is approximately 0.07 L/s. The column diameter is 0.044 m, resulting in a cross-sectional area of 0.00152 m². Using Equation 5-1, the gas velocity was determined to be 0.046 m/s which is just above 0.035 m/s. This means that even at the maximum flow rate provided by the aquarium air pumps, the bubbles should maintain a transitional homogeneous flow regime.

EQUATION 5-1: GAS VELOCITY

$$v = Q * A \tag{1}$$

- v = gas velocity
- Q = volumetric flow rate
- A = cross sectional area

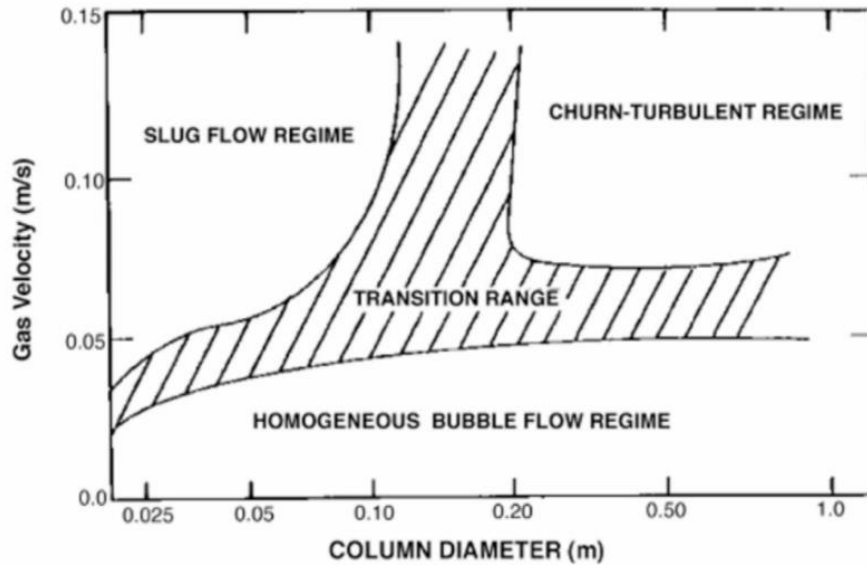


FIGURE 5-2: FLOW REGIME [4]

The estimated mass transfer coefficient which affects the rate of mass transfer for the bubble column was determined in section 3.2. This was determined based on the bubble size selection and estimated gas flow. The k_{LA} was determined to be 0.051/s.

The final projected design parameters are shown in Table 5-1 for the PW. The gas parameters such as flow rate and toluene concentration will be determined through bench scale model testing. The flow rate describes the water in and out based on the filling and emptying mechanism. The volume shows the required liquid volume to be treated. The cross-sectional area shows the available space for water to flow. The velocity is calculated based on the cross-sectional area. Finally, the concentration of toluene shows the required concentrations for treatment.

TABLE 5-1: DESIGN PARAMETERS

	PW_{in}		PW_{col}		PW_{out}	
Flow Rate	0.00069	<i>m³/s</i>	0	<i>m³/s</i>	0.00284	<i>m³/s</i>
Volume	0.00114	<i>m³</i>	0.00114	<i>m³</i>	0.00114	<i>m³</i>
Time	1.6	<i>seconds</i>	Experimental		0.4	<i>seconds</i>
Cross Sectional Area	0.00029	<i>m²</i>	0.00155	<i>m²</i>	0.00155	<i>m²</i>
Velocity	2.435	<i>m/s</i>	0	<i>m/s</i>	1.829	<i>m/s</i>
Temperature	Ambient		Ambient		Ambient	
Concentration Toluene	50	<i>mg/L</i>	2-50	<i>mg/L</i>	2	<i>mg/L</i>

5.3 ADSORPTION PROCESS DESIGN

The adsorption capacity of the selected materials was similar. Therefore, the team decided on the most sustainable option, biochar. Biochar has a high removal efficiency. The amount of biochar is needed in the column to ensure there are minimal VOC emissions was determined in the laboratory results shown in section 6.2. The biochar adsorption column is attached to the bubble column using flexible tubing. VOC emissions were tested using this method and described in the prototype lab results section.

5.4 PIPING AND INSTRUMENTATION DIAGRAM

The final bench-scale model design is shown in Appendix D. The final P&ID is shown in Figure 5-3 below. The experimental parameters are to be determined following the testing detailed below.

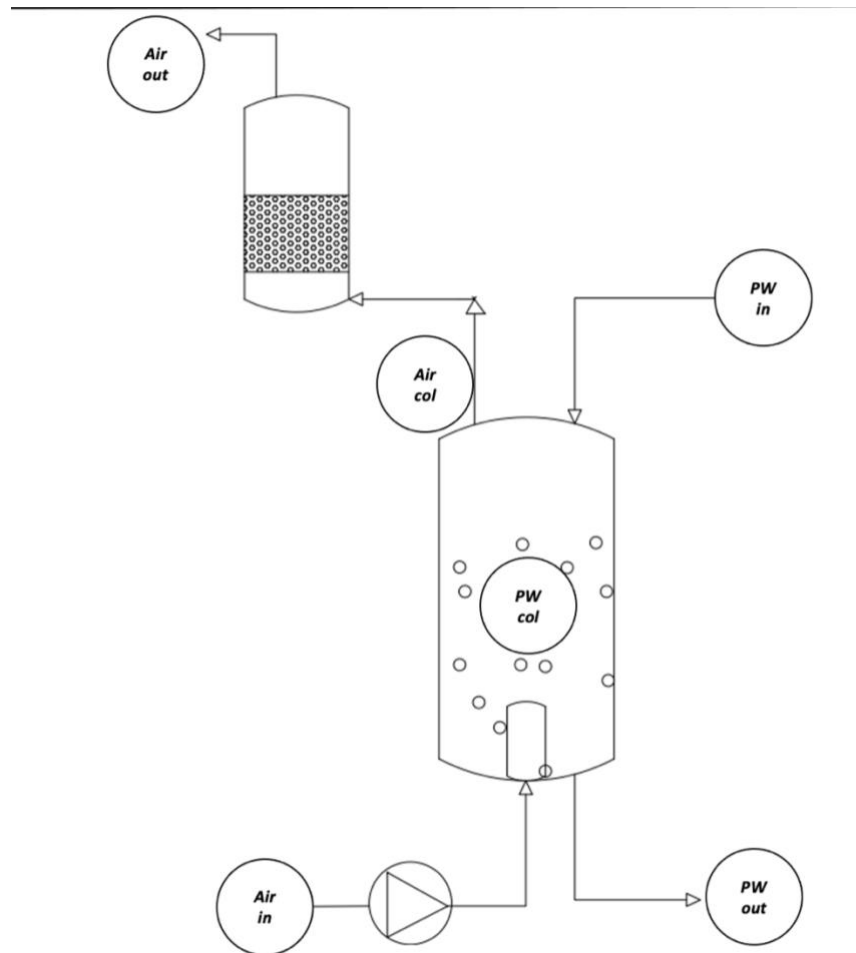


FIGURE 5-3: P&ID OF THE BENCH SCALE SYSTEM

Tables 5-2 and 5-3 below show the mass balances for toluene in the liquid and air in the final bench scale design of the bubble and adsorption columns.

TABLE 5-2: LIQUID MASS BALANCE

Parameter	PW in	PW col	PW out
Toluene Concentration (mmol/L)	0.54265	0.02171	0.02171
Air Volumetric Flow (L/min)	N/A	N/A	N/A
Liquid Volumetric Flow (L/min)	4.5	0.0	22.7
Toluene Mass Rate (mg/min)	227.12	0.00	45.42
Absolute Pressure (atm)	1	1	1
Temperature (°F)	Ambient	Ambient	Ambient
Duration (min)	0.25	15.62	0.05
Volume (L)	1.14	1.14	1.14
Total Toluene (mmol)	0.616	0.025	0.025

TABLE 5-3: GAS MASS BALANCE

	Air in	Air col	Air out
Toluene Concentration (mmol/L)	0.00000	0.00757	0.00000
Air Volumetric Flow (L/min)	5	5	5
Liquid Volumetric Flow (L/min)	N/A	N/A	N/A
Toluene Mass Rate (mg/min)	0.00	3.49	0.00
Absolute Pressure (atm)	1	1	1
Temperature (°F)	Ambient	Ambient	Ambient
Duration (min)	15.62	0.50	15.62
Volume (L)	78.10	2.49	78.10
Total Toluene (mmol)	0.000	0.592	0.000

6.0 PROTOTYPE LAB RESULTS

The main aspects of testing completed include VOC air emission testing, aqueous VOC testing, and SPOT testing.

6.1 VOC AIR EMISSION TESTING

To determine the adsorption capacity of biochar, the team conducted adsorption isotherm tests on two different biochar products utilizing a constant volume gas method. One biochar, biochar A, is pyrolyzed from dead tree biomass from forest floors, and the other,

biochar B, from wastewater sludge. Unfortunately, due to experimental problems and equipment inconsistencies the team was not able to get good isotherm data for biochar A, and biochar B only had 3 good data points fitting an isotherm model. Figure 6-1 below shows the Langmuir isotherm fit for biochar B.

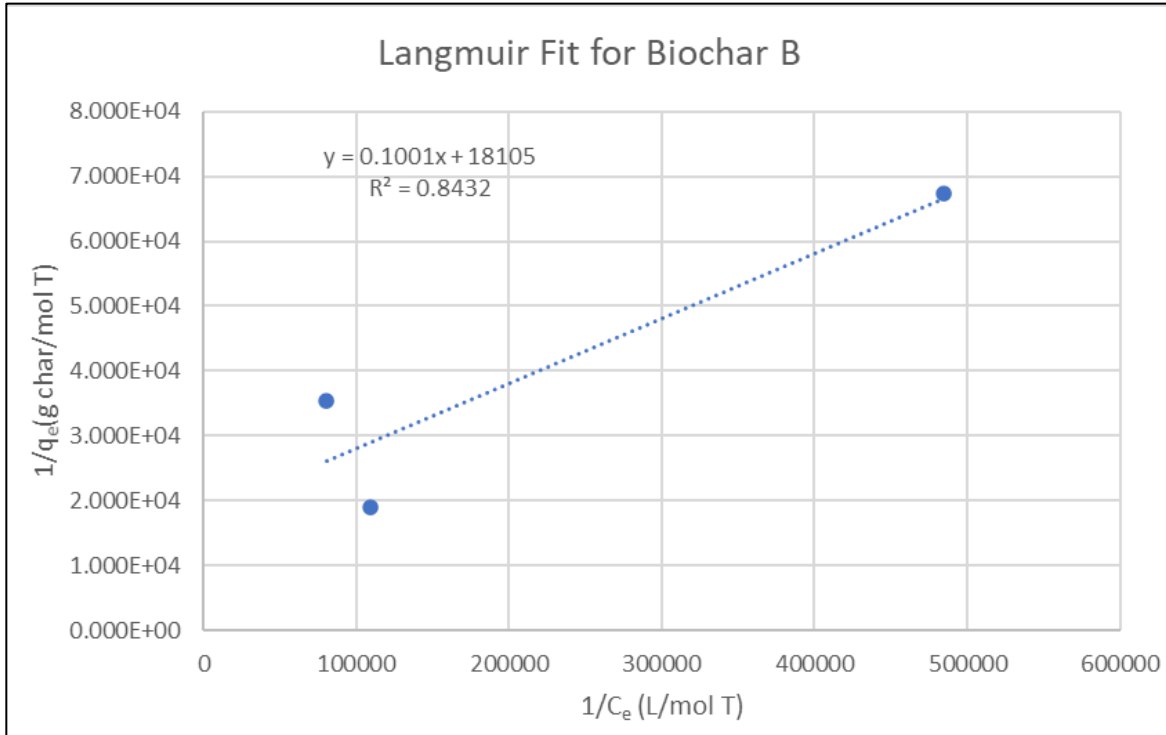


FIGURE 6-1: LANGMUIR ISOTHERM MODEL

Langmuir, Freundlich, Henry, Temkin, Elovich, and Jovanovic isotherm models were considered. Upon graphing the various models, the highest R squared value, 0.8432, was shown in the Langmuir model. A high R squared value is indicative of a high regression correlation within the data. The R squared values for the different isotherm models are shown in Table 6-1 for biochar B. Biochar A couldn't be fitted to any isotherm models because the capacity trendlines sloped down which is not correct.

TABLE 6-1: BIOCHAR B ISOTHERM MODEL COMPARISON

Isoterm Model	R²
Langmuir	0.8432297
Freundlich	0.6055028
Henry	0.2815555
Temkin	0.430882
Elovich	0.000159
Jovanovic	0.4496587

Using the Langmuir model for biochar B, and experimental data from tests in the next section, the adsorption capacities for both biochars were approximated. Table 6-2 below shows the approximated adsorption capacities.

TABLE 6-2: ADSORPTION CAPACITIES

Material	Capacity	Units
Biochar A	0.912	mg T/g char
Biochar B	0.175	mg T/g char

Biochar A has a significantly higher adsorption capacity, which is likely due to the much larger particle sizes of biochar B. Biochar B would work for this system as well, but it would be better if it was ground into smaller particles. From this point on in the design, biochar A was used for the design since it has a higher adsorption capacity.

VOC air emission testing was conducted to determine the concentration of toluene exiting the bubble column. This testing was completed on the column without the use of treatment from biochar to determine the toluene vapor mass rate before a filter. The testing was also conducted with the use of biochar to ensure the treatment process was adequate. The data shown in Table 6-3 was determined using a Tedlar bag and a GC to determine concentrations. The Tedlar sample bag has a volume of 0.5 L.

Air samples were taken using a biochar product as the adsorbent material. Samples were taken both with and without the biochar filter to calculate the estimated removal efficiency. Table 6-3 shows carbon use, sample ID, peak area measured with the GC, water equilibrium concentrations, molar fractions for water and air, and the final concentration of toluene in air. Sample T1 was eliminated due to a leak in the column piping.

TABLE 6-3: VOC AIR EMISSION TESTING

Biochar	Sample	Peak Area	H₂O Conc.	x_A	y_A	C_A air	air T in vial
yes/no	(#)	(mV-s)	(mg/L)	mol T/mol H ₂ O	mol T/mol air	mol T/ L air	mol
no	T1	53996	88.137	1.728E-05	8.638E-03	3.653E-04	1.827E-04
no	T2	11648	19.013	3.727E-06	1.863E-03	7.881E-05	3.940E-05
no	T3	10418	17.005	3.333E-06	1.667E-03	7.048E-05	3.524E-05
no	T4	9736	15.892	3.115E-06	1.557E-03	6.587E-05	3.293E-05
yes	T5	1686	2.752	5.394E-07	2.697E-04	1.141E-05	5.703E-06
yes	T6	0	0.000	0.000E+00	0.000E+00	0.000E+00	0.000E+00
yes	T7	1365	2.228	4.367E-07	2.184E-04	9.235E-06	4.618E-06

The average of samples T2, T3, and T4 was taken to determine the concentration of toluene exhausted from the column without the use of activated carbon. The removal efficiency was then calculated for samples T5, T6, and T7 and is shown in Table 6-4. The removal efficiency, using 3.275 grams of biochar, was determined to be above 80%. The desired concentration of toluene leaving the adsorption column was 0, so additional biochar was added to achieve a final biochar mass of 9.2 grams.

TABLE 6-4: AIR REMOVAL EFFICIENCIES

Sample (#)	Removal Efficiency (%)
T5	84.1%
T7	87.1%
T6	100%

6.2 AQUEOUS VOC TESTING

The required effluent water concentration is 2 ppm or 2 mg/L of toluene, reduced from a starting concentration of 50 mg/L. This means a removal of 96% is required. The produced water was tested and determined to have an initial toluene concentration of 167.15 mg/L which is higher than the proposed concentration of 50 mg/L. Based on the final toluene concentrations, however, a removal of 96% was achieved between 15-20 minutes of treatment which indicates the column works as desired. This fact is shown in Table 6-5.

TABLE 6-5: AQUEOUS VOC TESTING RESULTS

Minutes	GC Injection (μL)	Sample (#)	Peak Area (mV-s)	H₂O Conc. (mg/L)
0	100	V4	102402	167.149
6.75	100	V5	5308	8.664
10	100	V6	6057	9.887
15	100	V7	4252	6.940
20	100	V8	3012	4.916
10	100	V9	2286	3.731

The treatment process was run for 6.75, 10, 15, and 20 minutes, sampling the water after the given duration. A duplicate sample was taken at 10 minutes when a different PW batch was run using the biochar air filter. The batch was not fresh, however, and the initial toluene concentration was likely lower which can explain the lower concentration in V9 compared to V6.

As shown in Figure 6-2, the removal efficiency of toluene was calculated for each of the treatment times. As treatment time increases, there is a direct relationship to the decrease of toluene concentration. The removal efficiency peaks at a treatment time of 20 minutes at 97.06%, however, a removal efficiency of only 96% is required.

Interpolating between the data points of 15 minutes and 20 minutes treatment time, an ideal treatment time to achieve a 96% removal efficiency is 15.6 minutes.

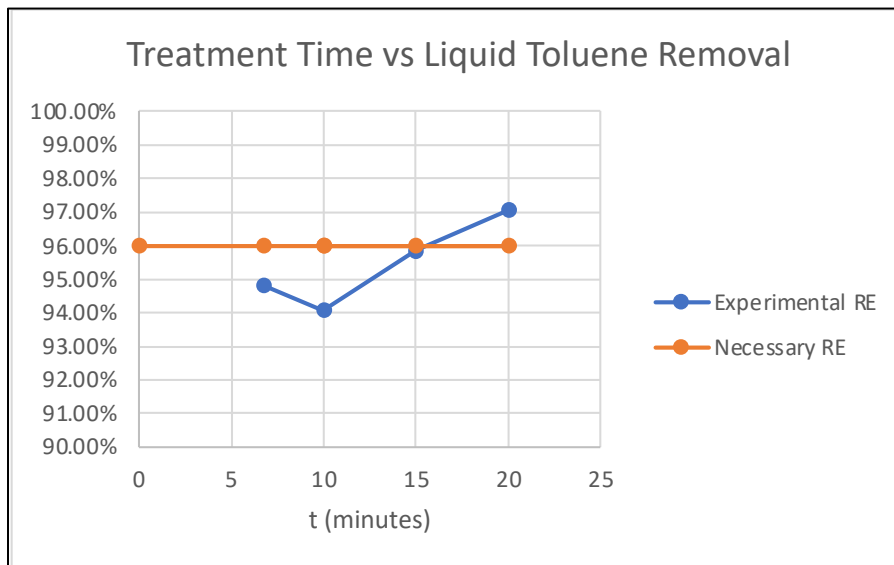


FIGURE 6-2: TREATMENT TIME VS LIQUID TOLUENE REMOVAL

6.3 SPOT TESTING

The required SPOT testing includes salinity, pH, oxidation reduction potential (ORP), and turbidity. Due to the equipment constraints of the Northern Arizona University Environmental Engineering Lab, only pH and turbidity were measured in the treated water. The results of the tests are shown in Table 6-6. This includes the results from untreated produced water as well as the results from a 20-minute treatment time.

TABLE 6-6: SPOT TESTING RESULTS

SPOT Testing	pH	Turbidity (NTU)
PW @ 0 min treatment	7.18	159
PW @ 20 min treatment	7.17	125

Table 6-6 shows that the treatment process does not significantly affect the pH level of the produced water. Table 6-6 also shows that a 20-minute treatment time will reduce the turbidity of the produced water.

7.0 BUSINESS PLAN

7.1 FULL-SCALE DESIGN DESCRIPTION

Northern Arizona University's design team has designed a system composed of five identical tanks to treat produced water in a full-scale design. The main design components consist of five bubble column batch reactors running in parallel. In Table 7-1 the basic overview of the final full-scale design is shown, with an AutoCAD rendition of the design shown in Figure 7-1.

TABLE 7-1: FULL-SCALE DESIGN

Number of Columns	5	columns
Column Diameter	1.270	m
Column Height	15.24	m
D:H	12	ratio
Pressure	3-5	Mpa
Temperature	Ambient	
Total Volume Available	96.53	m ³
Cross-Sectional Area	1.267	m ²
Flow Water	7949	m ³ /day
Number of Batches	82.35	batches/day
Number of Batches per Hour	3.431	batches/hour
Tank Filling Time	0.900	minutes
Tank Emptying Time	0.900	minutes
Treatment Time	17.49	minutes
Total Time Set for Each Batch	19.29	minutes
Water Volume per Batch	96.53	m ³

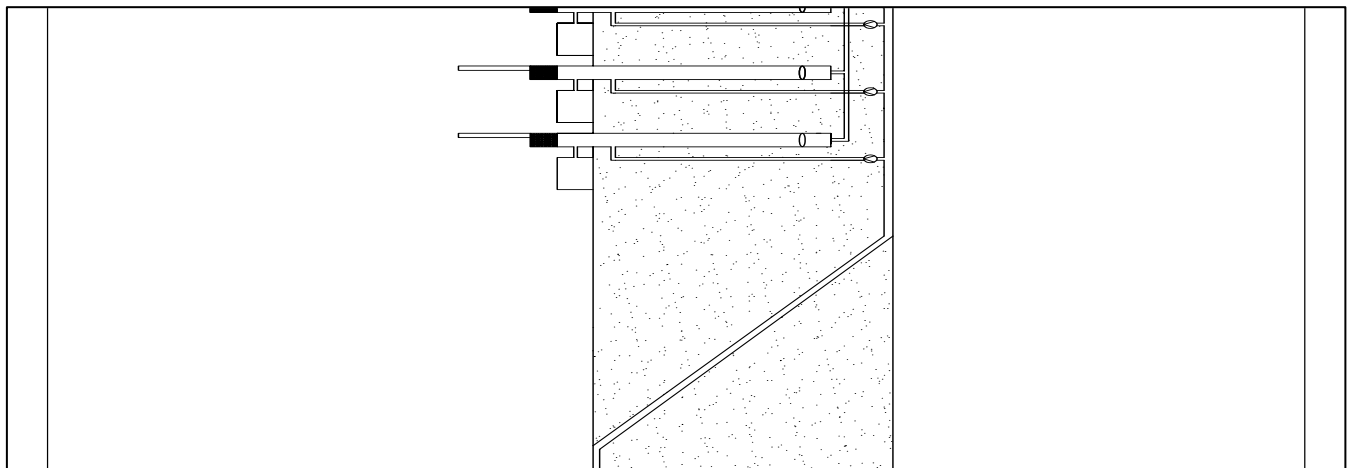


FIGURE 7-1: FULL-SCALE TREATMENT DESIGN

Water exits the hydraulic fracturing plant at a rate of 50,000 bbl/day. The water is then pumped into a water main pipe using a 2,100,000 gal/day pump. The water is then

branched off into five tapping connections where water flows into the 5 bubble column reactors. The water is pumped into the bubble column reactors at a height of 16 m where the max fill is 15.24 m. Once the max fill is achieved, the pumps are shut off.

The bubble column reactor will be designed like an aeration basin. The bubbles for mass transfer are produced via an electric aeration system at a rate of 120 cfm to maintain homogenous flow. The aeration system will produce bubbles at the bottom of the bubble column reactor. Experimentally, the process was found to take 15.6 minutes per batch of 96.53 m³ of water to treat all the produced water in a day. This means that the equipment will be running for 21.44 hours per day, allowing time for tanks filling and emptying. The adsorption bed will be attached to the top of the bubble column reactors and will remove VOCs from the gas stream before entering the outside air. A mass of 368 lbs/year of biochar will be needed to ensure air emission requirements are met. Table 7-2 below shows the mass and energy balances of a single bubble column reactor in this system, with labels referring to the same process locations as the bench scale model.

TABLE 7-2: MASS AND ENERGY BALANCE OF A SINGLE FULL SCALE BUBBLE COLUMN

	PW in	PW col	PW out	Air in	Air col	Air out
Toluene Concentration (mol/m ³)	0.543	0.022	0.022	0.000	0.189	0.000
Air Volumetric Flow (m ³ /min)	N/A	N/A	N/A	3.398	3.398	3.398
Liquid Volumetric Flow (L/min)	4.542	0.000	22.712	N/A	N/A	N/A
Toluene Mass Rate (g/min)	227.125	0.000	45.425	0.000	59.326	0.000
Absolute Pressure (atm)	1	1	1	1	1	1
Temperature (°F)	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
Duration (min)	0.900	15.620	0.900	15.620	0.283	15.620
Volume (m ³)	19.306	19.306	19.306	53.077	0.963	53.077
Total Toluene (mol)	10.476	0.419	0.419	0.000	10.05716	0.000
Energy (kW-h)	120.700	N/A	120.700	140.700	N/A	140.700

7.2 CAPEX AND OPEX

The total capital cost (CAPEX) for the installation of the proposed design was analyzed in Table 8-3 below. The total capital cost for installation is estimated to be \$783,850. These

costs were obtained in April 2022. The breakdown of installation and labor costs is an estimate. Therefore, specific costs and timeframe is not known. Multiple sources were referenced to determine the costs, however, because of the specific needs of the project, often only one vendor was needed to quote. The results of this are shown in Table 8-3.

TABLE 7-3: FULL-SCALE CAPEX COSTS

Item	Quantity	Units	Cost	Total Cost
Adsorption Columns [19]	1	ton	\$1,712	\$1,712
Tank [20]	5	tanks	\$8,500	\$42,500
Pump (364.58 gpm) [21]	5	pumps	\$5,692	\$28,462
Pump (1458.32 gpm) [21]	2	pumps	\$21,000	\$42,000
Electric Aeration System [22]	5	systems	\$1,831	\$9,155
Adsorption Tower [23]	5	containers	\$1,050	\$5,250
Pipe 1 (PVC, diameter 24 in) [20]	140	m	\$16	\$2,265
Pipe 2 (PVC, diameter 24 in) [20]	80	m	\$16	\$1,294
Aeration System Housing [24]	5	units	\$242	\$1,210
Installation and Labor Cost (estimate)	5	units/hole	\$130,000	\$650,000
Total Construction Cost				\$783,850

Upon completion of the capital install, the operating costs (OPEX) were considered in Table 8-4. The total operating cost for this process was found to be \$0.16/bbl of PW or \$2,920,000 per year.

TABLE 7-4: FULL-SCALE OPEX COSTS

Staff Labor [25]	70	\$/hr
	3	operators
	1680	\$/day
	0.03	\$/bbl
Solids Disposal Cost [25]	50	\$/ton
	134.2	tons/year
	6710	\$/year
	0.0004	\$/bbl
Adsorption Material Purchasing [23]	1712	\$/ton
	367.75	lbs/year
	315	\$/year
	0.00002	\$/bbl
Electricity Cost [25]	0.09	\$/kWh
	26.6	kWh
Energy Requirements [25]	0.11	\$/bbl
	1.27	kWh/bbl
Natural Gas Cost [26]	13.27	\$/MCF
	N/A	\$/bbl
Total New Operating Costs	0.16	\$/bbl

7.3 IMPLEMENTATION SCHEDULE

The project schedule is shown in Figure 7-2 for a start date of May 2022. The estimated project completion would occur over 1 to 2 years including community outreach and construction.

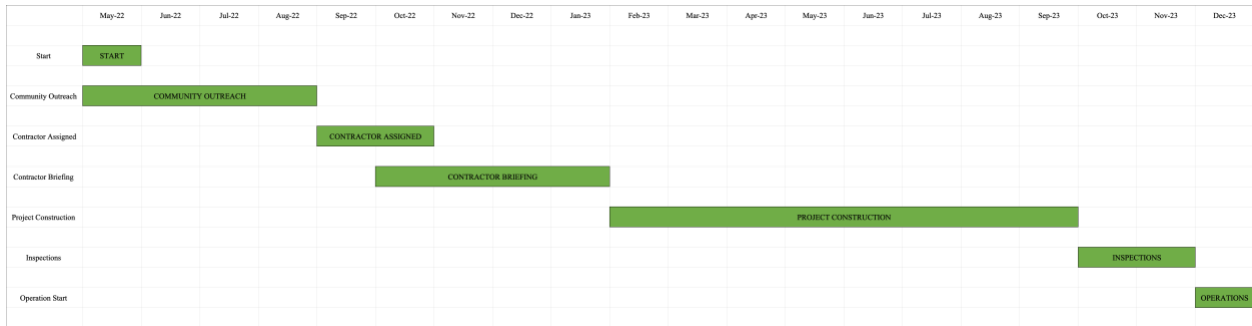


FIGURE 7-2: IMPLEMENTATION SCHEDULE FOR THE FULL-SCALE DESIGN

7.4 INVESTMENT PLAN

Based on the associated capital and operational costs of the design, the project was analyzed at a broader level to estimate the potential for earnings if a company perused this technology.

The target market, or customer, that this design would be marketed to is the hydraulic fracturing market. This is because those companies are now required to comply with new regulations and lack the technology to meet this goal. In addition, this design will help hydraulic fracturing companies to reuse water and therefore lower their operational costs. In the United States, there are about 300,000 hydraulically fractured wells which provides a large market to target. The total addressable market in this regard can be estimated to be a \$3,750,000,000 opportunity. Since this project was targeted in the Southwest, the Serviceable Addressable Market is a \$1,957,500,000 opportunity. Based on the reduction of costs associated with this technology, specifically \$0.25 per barrel to \$0.16 per barrel, results in a share of market of 0.36%.

8.0 WASTE REPORT

8.1 WASTE GENERATION

Hazardous waste in the form of biochar saturated with toluene will need to be replaced often. This is generated at a mass of 2.56 pounds of biochar every 61 hours in a full-scale

system. A mass of 134.19 tons/year of biochar will be used at this rate. The hazardous biochar waste will be contaminated with toluene and will require either regeneration or disposal.

Construction waste will be present when installing the treatment process. No hazardous waste will be present. The cost of disposal is included in the labor and installation costs.

8.2 WASTE DISPOSAL

Adsorption material solid waste will contain toluene removed from the air stream and will need to be disposed of according to local regulations where this system is implemented.

Construction waste will be disposed of by the contractor. The cost of disposal is included in the labor and installation estimate.

9.0 ADHERENCE TO HEALTH, SAFETY, AND ENVIRONMENTAL REGULATIONS

The main purpose of this project was to create a process that would allow the recycling of produced water to meet new imposing regulations. The regulation that needed to be met was two tons of VOC per year per PW impoundment based on the potential to emit. This regulation implemented by the EPA and clean air act (CAA) is limiting the ability to recycle produced water by way of an open surface PW impoundment facility. By utilizing this treatment process, companies would be able to effectively clear their produced water of enough VOCs to meet regulations that would allow the storage of PW within an open surface impoundment.

The process for cleaning the PW of VOCs also comes with a host of other regulations it must meet as well. To ensure the health and safety of workers operating the facility, OSHA requires a general industry limit of toluene per 8-hour workday to be no more than 200ppm average, 300ppm ceiling (15 minutes), and 500ppm maximum (10 minutes) [27]. To ensure proper indoor air quality, adequate ventilation should be provided within enclosed worker areas near the treatment process. All other worker conditions for oil and gas well drilling and servicing

operations are covered by 29 CFR 1910. If a specific workplace hazard is not covered by this code, section 5(a)(I) (“General Duty Clause”) of the OSHA act applies [27]. Construction of the processing site also needs to meet all OSHA regulations regarding the construction of oil and gas site preparation covered in 29 CFR 1926 [27].

On a federal level, this proposed design would need to abide by EPA regulations. These regulations are associated with both water and air pollution guidelines as the recycling of the PW may involve treated water discharge which is subject to the National Pollutant Discharge Elimination System (NPDES). Since toluene is a hazardous air pollutant (HAP) the proposed facility would be governed by National Emissions Standards for Hazardous Air Pollutants (NESHAP) and would need to complete compliance monitoring [28]. Toluene also can react with sunlight and produce tropospheric ozone which is a criteria air pollutant as described by the National Ambient Air Quality Standards (NAAQS). This would mean that the process would have to limit the toluene emitted from the PW treatment process to such a level as to stay within attainment levels of 70 ppb ozone [29]. The storage vessel for the PW itself would also be regulated by the NSPS subpart Kb which regulates the Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984 [30]. Additionally, the EPA requires regular inspection of equipment that is used in the oil and natural gas industry. Inspections need to check for leaks or “fugitive emissions” within the system and should be done at least once every quarter [28]. On state and local levels here in Arizona, permitting for the produced water impoundment would need to be obtained by the Arizona Office of the State Engineer (OSE) and any construction permits would also need to be obtained through local agencies. Since there will be a potential to emit HAPs, a class I permit would be required from the Arizona Department of Environmental Quality [28]. Other more local county- and city-wide permits may be needed depending on where in the state of Arizona the site would be located.

10.0 COMMUNITY RELATIONS AND ACCEPTANCE PLAN

10.1 COMMUNITY RELATIONS PLAN

The potential for release of VOC emissions throughout the process of treating produced water creates a need to involve the local community, as there is potential to negatively impact the health of people and the environment. The purpose of this plan is to facilitate communication between the project sponsor and the local population of a region for which a produced water treatment process is best suited for.

Outreach via various social media outlets will provide contact information for the project sponsor with a line dedicated to questions and concerns regarding the implementation of produced water treatment. This social media strategy will also relay major news releases and advertise details of both public meetings and notices. Public meetings will be scheduled and held to present information to the local population and gauge the level of interest in the project while also receiving feedback from those in attendance regarding questions and concerns. A community mailing list will be established, and the public meetings used as a place for those interested to provide contact information to be included. This mailing list will reiterate the same information as the social media outreach but will include additional documentation such as newsletters, fact sheets, and invitations for community stakeholders to participate in interviews to address community concerns and interests. Each written article will be added to a website dedicated to the project sponsor's effort to install produced water treatment and allow for all documentation to be continuously updated with the most relevant data/information.

10.2 COMMUNITY ACCEPTANCE PLAN

Public Involvement during Project Development: Scoping meeting, meetings with local agencies and special-interest groups, tribal meetings, public hearings, project website, newsletters.

Public Involvement during Design: Meetings with local agencies, special-interest groups, and tribal committees, public information meetings, project website, newsletters.

Public Involvement during Construction: Meetings with local agencies, special-interest groups, and tribal committees, public information meetings, project website, newsletters, provide up-to-date information to minimize disruption to the communities' residents and businesses while construction is underway.

Public Involvement during Operations/Maintenance: Public meetings, project website, newsletters, informing the local populace of any work zones/detours/temporary access impact caused by operation and maintenance.

11.0 SUMMARY OF ENGINEERING WORK

Overall, the project was carried out in a similar process to the proposed schedule. The proposed and final Gantt chart schedules are shown in Appendix E.

The first major delay in the project was the shipment and ordering of materials to build the bench scale model. This delay happened mainly because of a lack of adequate planning. It also occurred because of Northern Arizona Universities robust ordering system. This delayed the team with creating the process flow diagram, gathering laboratory data, and construction. The second major delay was related to the model redesign and was also caused by the slow process of ordering and shipping materials.

Although other tasks were delayed, all the deliverable deadlines in task 8 were completed on time which ensured all the tasks were completed and project requirements met. The team worked hard to ensure these deadlines were met which resulted in a successful project.

12.0 SUMMARY OF ENGINEERING COSTS

The project was carried out while tracking the hours for each of the four staff members, Senior Engineer, Engineer, Lab Technician, and Intern. The summary of hours proposed for each task

during the duration of the project is shown in Table 12-1. The hours proposed per position are summarized in Table 12-2.

TABLE 12-1: PROPOSED TASK HOURS

Task Name	SENG (hours)	ENG (hours)	TECH (hours)	INT (hours)	Task Total Hours
Task 1: Competition Preparation	2	0	40	17	59
Task 2: Analyze Treatment Options	6	60	76	48	190
Task 3: Bench-Scale Model Design	8	40	12	48	108
Task 4: Bench-Scale Model Fabrication and Testing	6	40	152	60	258
Task 5: Full-Scale Design	4	44	0	32	80
Task 6: Techno-Economic Analysis	6	20	0	26	52
Task 7: Impacts Analysis	6	12	0	0	18
Task 8: Deliverables	18	16	12	24	70
Task 9: Project Management	12	36	12	36	96
Total Hours	68	268	304	291	931

TABLE 12-2: PROPOSED STAFFING HOURS

Staffing Hours Summary	
Position	Hours
Senior Engineer	68
Engineer	268
Lab Technician	304
Engineering Intern	291
Total Hours	931

The actual hours broken down by task and then by staff member are shown in Table 12-3 and 12-4.

TABLE 12-3: ACTUAL TASK HOURS

Task Name	SENG (hours)	ENG (hours)	TECH (hours)	INT (hours)	Task Total Hours
Task 1 Competition Preparation	0	0	28.5	1.25	29.75
Task 2: Analyze Treatment Options	0	21	78.5	28	107
Task 3: Bench Scale Model Design	0	18	12	20	50
Task 4: Fabrication of Bench Scale Model	0	6.75	45.25	7.25	59.25
Task 5 Full-Scale Design	0	12.5	1.25	3	16.75
Task 6: Techno-Economic Analysis	0	0	0	28.25	28.25
Task 7: Impacts Analysis	0	0	0	3	3
Task 8: Project Deliverables	113	138.3	162.5	253.5	667.3
Task 9: Project Management	14.5	14.75	6	13.75	49
Total Hours	1043.65				

TABLE 12-4: ACTUAL STAFFING HOURS

Staffing Hours Summary	
Position	Hours
Senior Engineer	127.75
Engineer	214.3
Lab Technician	334.1
Engineering Intern	367.5
Total Hours	1043.65

The key difference between the proposed hours versus the actual hours is the addition of labor. The proposed hours summarized to 931 hours while the team ended up completing 1043 hours to complete the project.

It is also important to note that the competition deliverables took longer than anticipated. This resulted in Task 8 taking up most of the hours. Bench scale testing and building took considerably less time than anticipated. Most of this was due to delays in materials and scheduling conflicts within the team. The reduced number of completed hours did not impact the quality of the project.

Table 12-5 shows the proposed and actual costs of engineering services. As the need to utilize the machine shop was not foreseen, the additional cost has been added into the subcontract section. Additionally, due to the delays, there was no time to send samples off for further testing so that cost has been removed from the subcontract section.

TABLE 12-5: PROPOSED COST OF SERVICES

Cost of Engineering Services				
<i>Personnel</i>	<i>Classification</i>	<i>Hours</i>	<i>Rate (\$/hr)</i>	<i>Cost (\$)</i>
	Senior Engineer	68	\$ 180	\$ 12,240
	Engineer	268	\$ 80	\$ 21,440
	Lab Technician	304	\$ 50	\$ 15,200
	Engineering Intern	291	\$ 25	\$ 7,275
1.0 Personnel Cost				\$ 56,155
2.0 Travel			Cost Per (\$)	Cost (\$)
Transportation	1 Van 4-Day Trip		\$65/day	\$ 260
Mileage	868 mi Roundtrip		\$0.38/mile	\$ 330
Hotel	3 Rooms 3 Nights		\$100/night	\$ 900
Per Diem	5 People 4 Days		\$19/day	\$ 380
Travel Cost				\$ 1,870
3.0 Lab Facilities				
	ENE Lab 10 Days		\$100/day	\$ 1,000
Lab Cost				\$ 1,000
4.0 Supplies				
	See Itemized Supplies List			\$ 1,984
Supplies Cost				\$ 1,984
5.0 Subcontract				
	Analytical, 5 samples		\$50/sample	\$ 250
Subcontract Cost				\$ 250
Total Cost				\$ 61,259

The mentioned changes in staffing hours are reflected in Table 12-6. From the proposed cost of services shown in Table 12-5, there is an increase in total cost by \$9,696.50.

TABLE 12-6: ACTUAL COST OF SERVICES

Cost of Engineering Services				
<i>Personnel</i>	<i>Classification</i>	<i>Hours</i>	<i>Rate (\$/hr)</i>	<i>Cost (\$)</i>
	Senior Engineer	127.75	\$ 180	\$ 22,995
	Engineer	214.3	\$ 80	\$ 17,144
	Lab Technician	334.1	\$ 50	\$ 16,705
	Engineering Intern	367.5	\$ 25	\$ 9,187.50
1.0 Personnel Cost				\$ 66,031.50
<i>2.0 Travel</i>			<i>Cost Per (\$)</i>	<i>Cost (\$)</i>
Transportation	1 Van 4-Day Trip		\$65/day	\$ 260
Mileage	868 mi Roundtrip		\$0.38/mile	\$ 330
Hotel	3 Rooms 3 Nights		\$100/night	\$ 900
Per Diem	5 People 4 Days		\$19/day	\$ 380
Travel Cost				\$ 1,870
<i>3.0 Lab Facilities</i>				
	ENE Lab 10 Days		\$100/day	\$ 1,000
Lab Cost				\$ 1,000
<i>4.0 Supplies</i>				
	See Itemized Supplies List			\$ 1,984
Supplies Cost				\$ 1,984
<i>5.0 Subcontract</i>				
	Machine Shop, Acrylic Cuts		\$70	\$ 70
Subcontract Cost				\$ 70
Total Cost				\$ 70,955.50

13.0 IMPACTS ANALYSIS

Triple bottom line analysis was conducted on this project to determine the social, economic, and environmental impacts of the design at a full-scale installation.

13.1 SOCIAL IMPACTS

The project potentially negatively effects the community in two ways. First, as commonly seen with new pollutant control measures, public backlash is common. With the installation of this design, VOCs would be a concern not only in the water but also in the air. In addition, during installation of the columns, the surrounding community would be impacted by new traffic patterns. However, these negative impacts can be mitigated by the use a community education plan and increased signage when construction occurs.

The implementation of this design would benefit the surrounding communities. First, hydraulic fracturing operations would be able to reuse produced water rather than pulling from additional freshwater resources. This means that the surrounding communities water resources are conserved. Next, through the community outreach plan, the community can gain knowledge about the treatment technology. This improves general overview education in the surrounding community and enhances the community's willingness for buy-in.

13.2 ECONOMIC IMPACTS

The project could potentially have negative economic effects in the form of increased road maintenance, industry competitors, and minimal operational job opportunities. The first effect, increased road maintenance, is caused by the increased traffic on local roads during construction. This can be avoided by minimizing the number of trips needed to transport supplies. Next, regarding the feasibility of the project, there are industry competitors which could out-sell this proposed design by offering a cheaper solution. This is addressed and avoided by offering a solution that is under the current costs of treatment of produced water. Finally, the installation of this solution could negatively impact economics by only offering three operational jobs. This does not increase the availability of labor in the surrounding areas.

In addition to mitigating the negative impacts, the project is also able to provide direct economic benefits. First, both construction and operational jobs will be provided. This is

especially apparent during the installation and first five years of the project. These jobs will stimulate the local economy. In addition, hydraulic fracturing companies will see a direct economic benefit by lowering operation and treatment costs to \$0.16 per barrel.

13.3 ENVIRONMENTAL IMPACTS

Install of this design may lead to potential negative environmental impacts. First, there is a possibility of discharge and emissions if the system malfunctions. This can be mitigated by continual monitoring and frequent maintenance inspections. In addition, this solution does not completely treat produced water to a reusable level. For example, the design does not account for oil components found in produced water. Additional capturing of these contaminants needs to be considered or implemented in the design to avoid a negative impact. However, this was out of scope for this project.

The design also offers many positive environmental impacts. First, the implementation of the design at full scale can conserve freshwater resources by allowing hydraulic fracturing operations to reuse produced water. Next, the treatment technology can reduce VOC emissions to under 2 tons potential to emit per year. This is a significant reduction in environmental pollution. Finally, the design incorporates a sustainable biochar in the absorption column.

14.0 CONCLUSION

The total initial capital cost for 5 columns is estimated to be \$173,848.90. This includes the total estimated cost for installation as well as materials. The columns will be operated for 21 hours a day, excluding filling and emptying times which makes this a 24-hour operation. The cost per barrel of VOC removal is \$0.16 including labor and maintenance. In addition, the main waste component of spent biochar can be disposed of for \$0.000010/bbl due to its high removal efficiency. A key component of this system is that 50,000 bbl/day of produced water can be treated for a minimal additional cost at \$0.16/bbl compared to the current cost of \$0.25/bbl. The final design is practical for

real-life implementation as shown in the economic analysis and resulting concentration values.

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APPENDIX A: ECONOMICS AND BUSINESS PLAN AUDIT

Nestlé Purina PetCare



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The below summarizes findings, recommendations, and questions from auditing the Economic and Business Plan contained in the report written by Rachel Sibayan, Daniel Herger, Gillian Neville, Hannah Robino, and Isaac Nance. In general, the team did a very thorough and robust job of reviewing the installation, procurement, and ongoing operational expenses associated with implementing their recommended technology.

- **General Questions and Recommendations for the Authors**
 - What are the identified risks (threats and opportunities) to the implementation schedule? What are possible mitigation strategies for these?
 - What are the identified risks (threats and opportunities) to the success of the technical design? What are the mitigation strategies for these?
 - How does the estimated capital and ongoing operational costs for this technology compare to its alternatives?
 - How do these costs equate to the estimated cost of treatment used in the decision matrix in Table 1? How were those costs estimated and ranked?
- **Other Specific Questions and Recommendations**
 - The "Total time for each set of batches" of 17.49 does not add to the sum of the "Tank filling time" and "Tank emptying time", barring inconsistency in the significant digits.
 - The "Number of batches" per day in Table 9 does not precisely match the equivalent figure calculated by multiplying the "Number of batches/hour" by 24 hours per day.
 - From where were the costs presented in Table 11 and Table 12 obtained? The source of these costs should be identified and/or cited.
 - The order of magnitude (approximation of precision) of the estimated costs should also be listed where known; i.e. +20%/-10%, +10%/-10%, etc.
 - In light of the inflationary environment being faced, a timeframe or date for when these cost estimates were obtained would be beneficial.
 - The installation and labor cost would be better presented as a breakdown of labor hours, if known.
 - A contingency percentage would be highly recommended when providing capital estimations; 5% to 20% is normal and depends upon the level of confidence of the estimated costs.
 - How was the implementation schedule calculated? Details about the sources for these estimations should be provided.
 - For costs of services (labor, solids disposal costs, etc.) were multiple providers consulted to achieve the most competitive pricing?

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Nestlé Purina PetCare Global Resources, Inc.



APPENDIX B: LEGAL AND REGULATORY ISSUES AUDIT

ESTABLISHED 2016

April 15, 2022

Dear Ms. Sibayan, Mr. Herger, Ms. Neville, Ms. Robino and Mr. Nance,

It has been a pleasure to provide an audit of your design for Controlling VOC Emissions from Produced Water Recycling in consideration of legal and regulatory compliance. Below is a summary of noted adherences and recommendations.

Overall, the proposed design offers a deliberate and effective solution for removal of toluene from produced water. The high efficiency of capture in the treatment process enables a reduction in air pollutant generation, meeting the objectives of the EPA's Clean Air Act and enabling compliance with the National Emission Standards for Hazardous Air Pollutants (NESHAP) for the oil and gas extraction industry.

As current regulations are aimed at reducing overall VOCs and air pollution generation, not just toluene, it is the recommendation of this reviewer that the design be additionally tested for effectiveness in capturing other chemicals known to be commonly associated with oil and natural gas development. Thus, enabling further design optimization for removal of a spectrum of air toxics and VOCs in produced water, as is to be expected in varying geographies and extraction methods found throughout the industry.

Waste products of this treatment process are spent biochar and produced water. Duly noted within the report are current OSHA limits for daily toluene exposure. While high level consideration is given to ventilation and waste storage containment needs to protect human health and safety, further design considerations are needed to allow for safe and rapid removal of spent biochar. Given the replacement rate of spent biochar for this treatment system (approximately 2.56 lbs per bed every 2.5 days), estimates on the concentration of toluene, or other toxic waste products in the spent biochar are needed to accurately assess exposure risk to waste handlers. Proper appraisal was given to municipal and regional environmental regulators for permitting for produced water impoundment.

Finally, an assessment for possible system failures and impact to human and environmental safety is also recommended. An understanding of the potential breakdowns in the system such that fail safes and monitoring can be designed and implemented will be critical to preventing any system leakages or worker injury. This could lead to further compliance requirements to relevant rules and regulations from both EPA and OSHA.

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In closing, the team provided a comprehensive review of relevant regulations pertaining to human and environmental health and safety. The treatment concept is well researched modeled and tested. It is encouraging to see such professionalism demonstrated by students. Keep up the good work and best of luck in your future endeavors!

Sincerely,

Sabrina Kleinman
Owner/Partner
EnviroPlan Partners, LLC
Ph: 720-446-0787
skleinman@enviroplanpartners.com

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APPENDIX C: MASS TRANSFER CALCULATION CONSTANTS

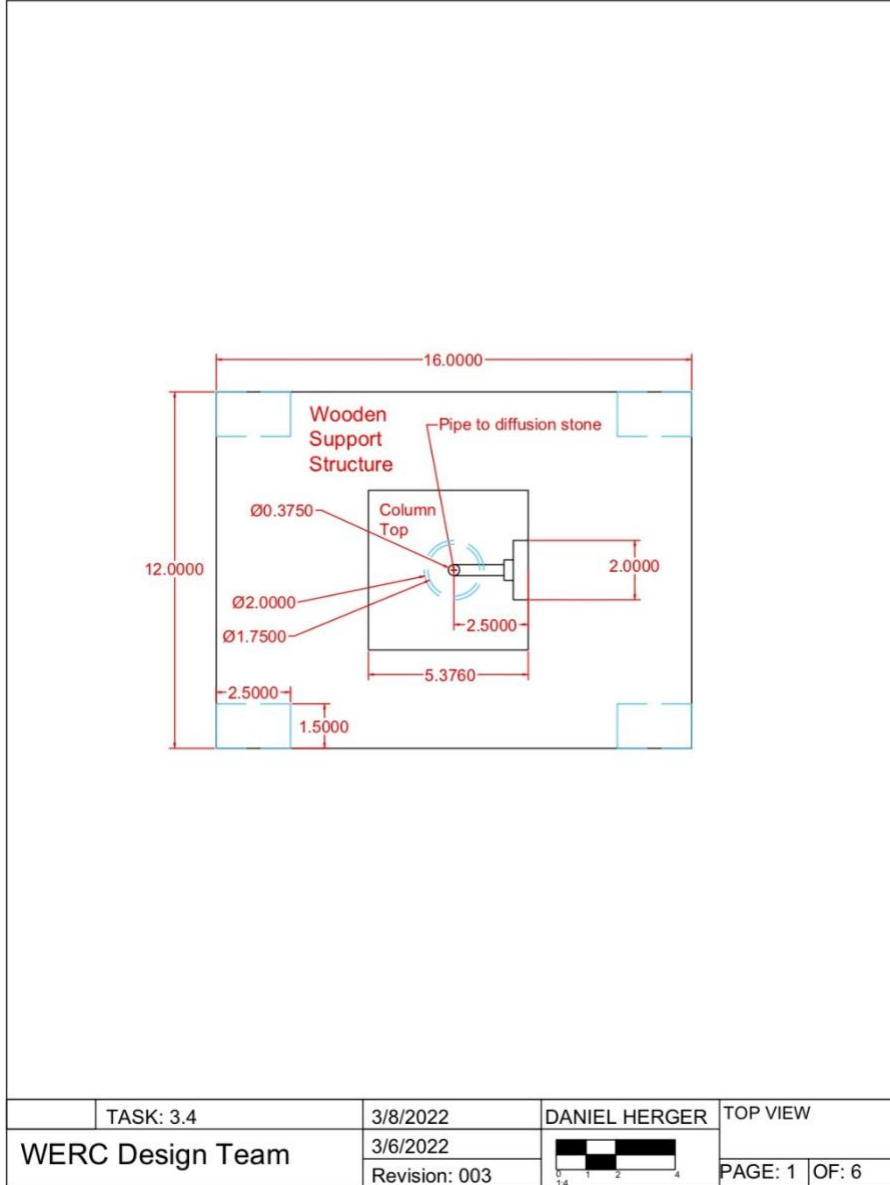
TABLE C-1: BUBBLE COLUMN CALCULATION CONSTANTS

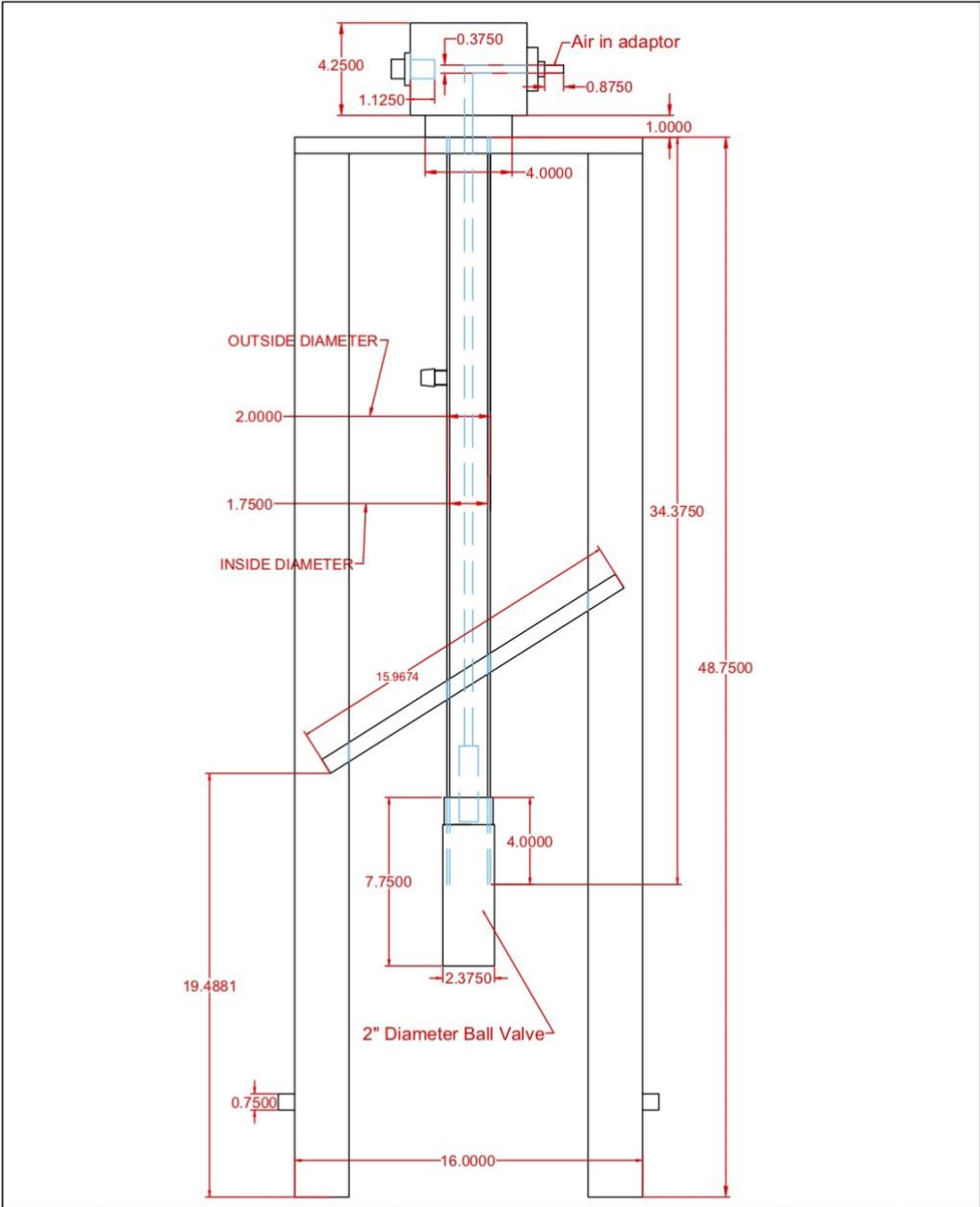
system temp, T	293.15	K
system pressure, P	0.8	atm
gravitational acceleration, g	9.81	m/s ²
water surface tension, σ_L	0.0728	N/m
gravitational acceleration, g	9.81	m/s ²
water density, ρ_L	998.2	kg/m ³
air density, ρ_G	1.225	kg/m ³
absolute viscosity, μ_L	9.82E-04	kg/m-s
absolute viscosity, μ_L	9.82E-04	N-s/m ²
diffusivity, D_{AB} @ system temp	8.13E-10	m ² /s
diffusivity, D_{AB} @ system temp	8.75E-09	ft ² /s
kinematic viscosity, ν	9.95E-07	m ² /s
toluene MW	92.15	g/mol
water MW	18.015	g/mol
air MW	28.9647	g/mol
Henry's constant, H	500	unitless
universal gas constant, R	0.0821	m ³ -atm/kmol-K
molar concentration of water	55.377	kgmol/m ³

TABLE C-2: PACKED TOWER PACKING MATERIAL COEFFICIENTS

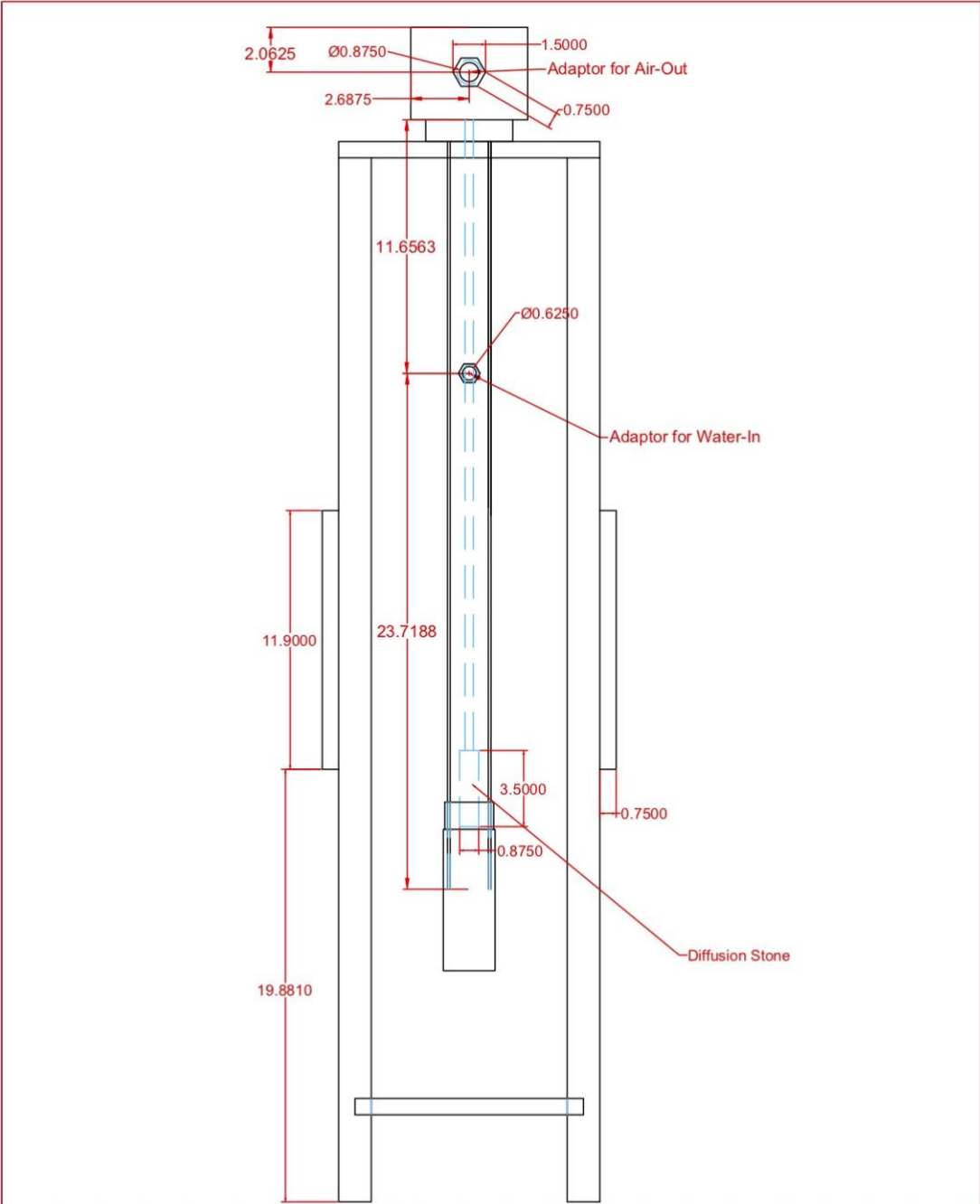
Packing	α	n
2.0 inch rings	80	0.22
1.5 inch rings	90	0.22
1.0 inch rings	100	0.22
0.5 inch rings	280	0.35
0.375 inch rings	550	0.46
1.5 inch saddles	160	0.28
1.0 inch saddles	170	0.28
0.375 inch saddles	150	0.28
3.0 inch spiral tiles	110	0.28

APPENDIX D: SHOP DRAWINGS

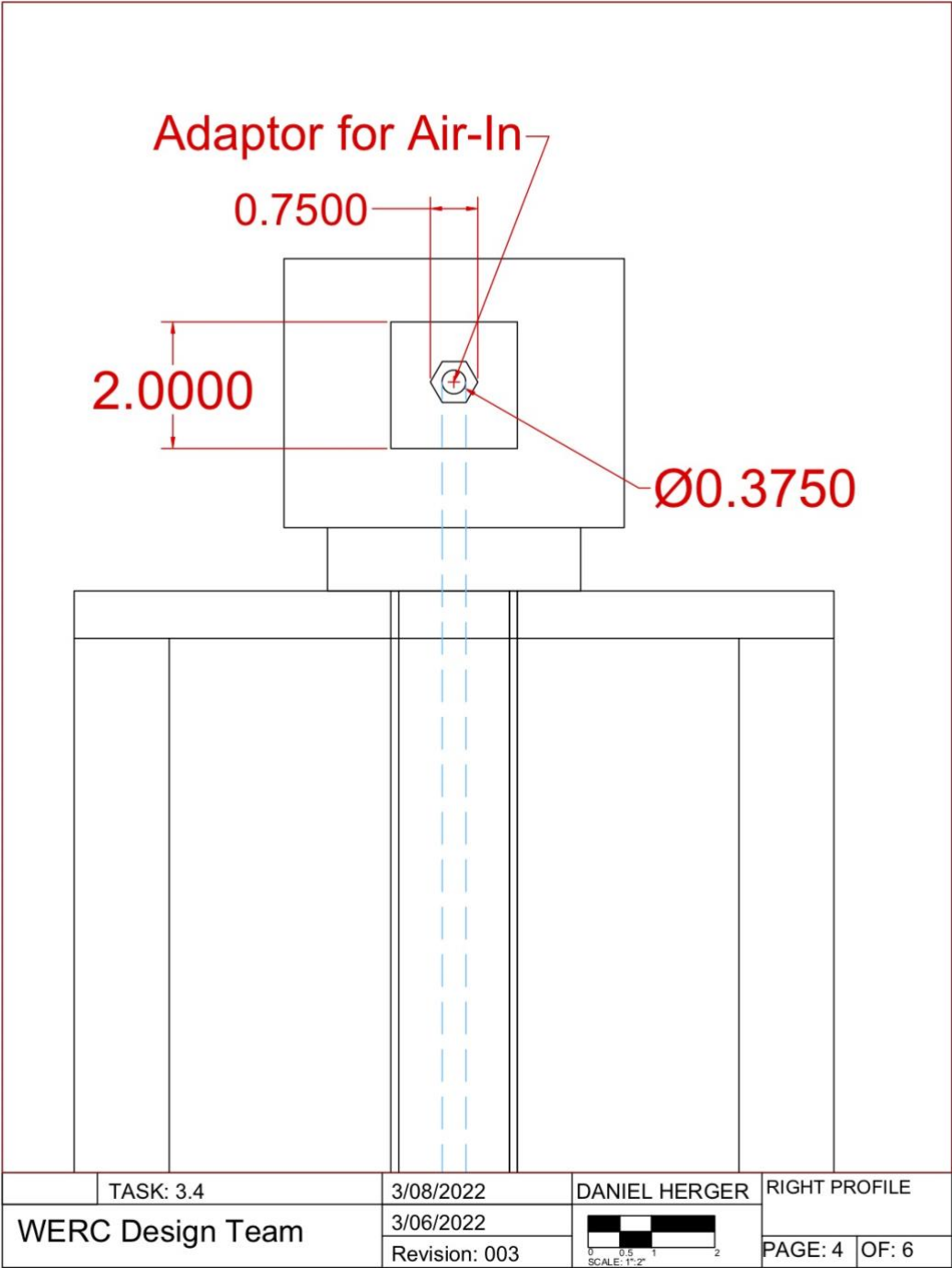


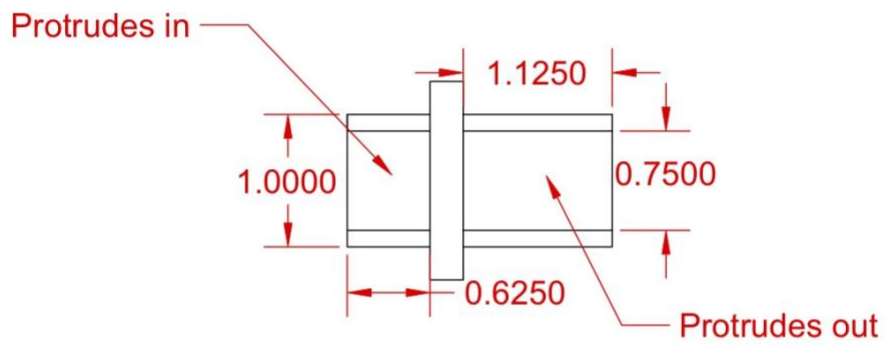



TASK: 3.4	3/08/2022	DANIEL HERGER	FRONT VIEW
WERC Design Team	3/06/2022	 SCALE: 1"=6"	PAGE: 2 OF: 6
	Revision: 003		

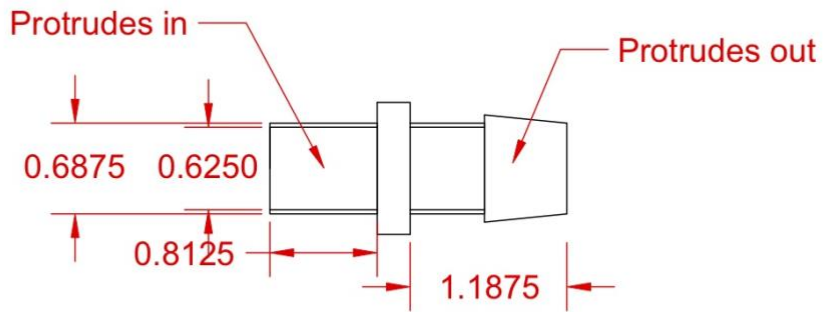


TASK: 3.4	3/08/2022	DANIEL HERGER	LEFT PROFILE	
WERC Design Team	3/06/2022	 SCALE: 1"=6"	PAGE: 3	OF: 6
	Revision: 003			



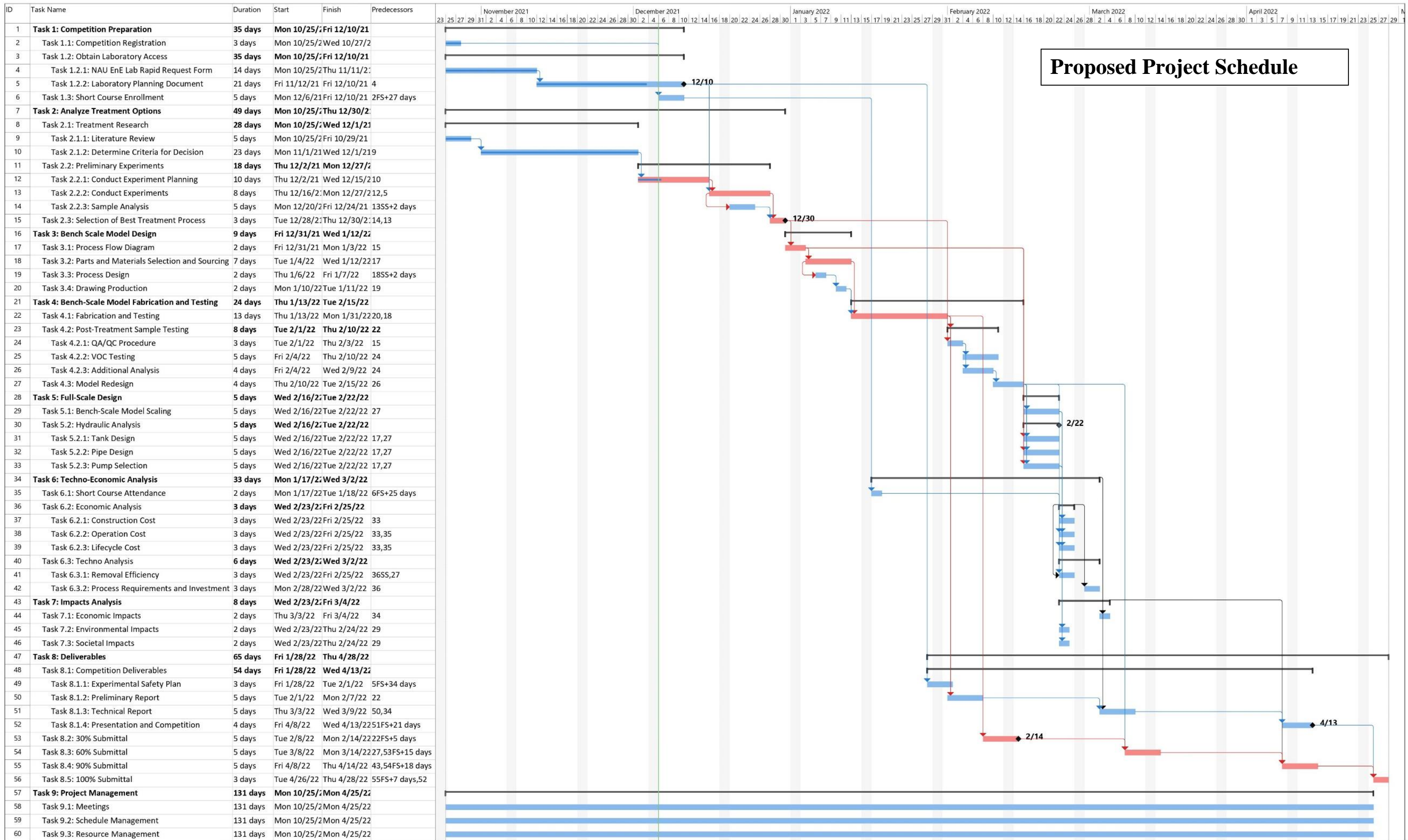


	TASK: 3.4	3/08/2022	DANIEL HERGER	ADAPTOR AIR OUT
WERC Design Team		3/06/2022	 SCALE: 1:1	PAGE: 5 OF: 6
		Revision: 003		



TASK: 3.4	3/08/2022	DANIEL HERGER	ADAPTOR WATER IN
WERC Design Team	3/06/2022	 SCALE: 1:1	PAGE: 6 OF: 6
	Revision: 003		

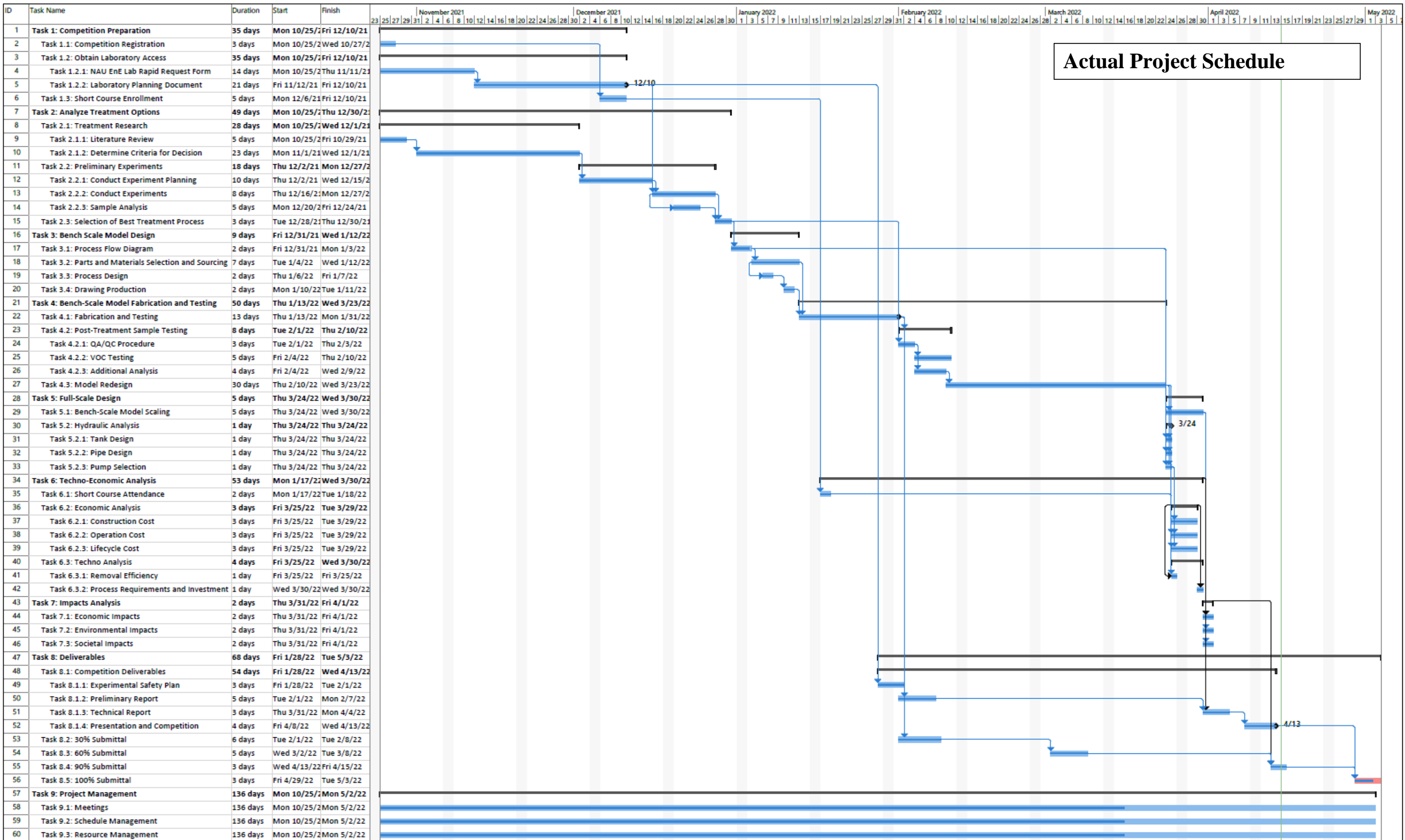
APPENDIX E: PROJECT SCHEDULE



Proposed Project Schedule

Project: WERC Gantt Chart New
Date: Mon 12/6/21

Task		Summary		Inactive Milestone		Duration-only		Start-only		External Milestone		Critical Split	
Split		Project Summary		Inactive Summary		Manual Summary Rollup		Finish-only		Deadline		Progress	
Milestone		Inactive Task		Manual Task		Manual Summary		External Tasks		Critical		Manual Progress	



Actual Project Schedule

Project: WERC Gantt Chart NEW
Date: Fri 4/15/22

Task	Summary	Inactive Milestone	Duration-only	Start-only	External Milestone	Critical Split
Split	Project Summary	Inactive Summary	Manual Summary Rollup	Finish-only	Deadline	Progress
Milestone	Inactive Task	Manual Task	Manual Summary	External Tasks	Critical	Manual Progress