

Construction of Prototype System for Directional Solvent Extraction
Desalination

by

Michael James Fowler

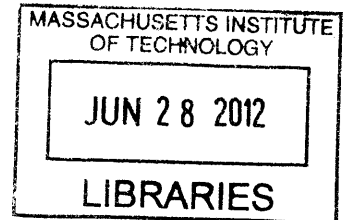
Submitted to the
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ABSTRACT

Directional solvent extraction has been demonstrated as a low temperature, membrane free desalination process. This method dissolves the water into an inexpensive, benign directional solvent, rejects the contaminants, then recovers pure water, and re-uses the solvent. In order to bring this technology closer to real world application, a continuous process prototype for a directional solvent extraction system was developed and tested. Octanoic acid was used as the solvent of choice, and a system capable of producing up to 7 gallons per day of fresh water was constructed. The system was tested to effectively desalinate the feed water, and the total system power was less than 7 kW.

The system was constructed and first tested to run fresh water and solvent through it. Fresh water was dissolved in and separated, as expected, from the solvent at a rate of about 2 gpd. Saline water containing 3.5% sodium chloride was then used as feedwater and the desalinated water was recovered at a rate of about 1 gpd with an average salinity of 0.175%.

Effective continuous operation of the directional solvent extraction prototype was demonstrated. Certain design improvements to increase efficiency, optimize component sizes, and decrease energy consumption are suggested. The demonstrated system has a wide range of applications, including production of fresh water from the sea, as well as, treatment of produced and flowback water from shale gas and oil extraction.

Thesis Supervisor: Gang Chen

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1. INTRODUCTION

As the global population increases, the supply of fresh water will struggle to meet demand, especially in developing countries. At current consumption rates, the world will be consuming about 90 percent of its available fresh water by 2025.^[3] Less than three percent of the earth's surface is fresh water, and two percent of that is frozen in glaciers. The oceans, however, cover seventy percent of the earth's surface and contain a seemingly endless supply of fresh water. Although seawater is not immediately consumable, desalination systems have been developed to tap into this vast supply of water. Improvements in desalination systems will help ease the approaching fresh water crisis. Current desalination systems can be divided into two general categories: membrane-based methods and evaporative methods.^[3]

Membrane methods rely on the use of a membrane to extract the salt from seawater and produce fresh water. The most popular example of this method is reverse osmosis.^[3] This process uses a semi permeable membrane that allows water, but not salt, to pass through it. The membrane has salt water on one side and fresh water on the other. The system will simultaneously attempt to reach equilibrium by balancing the osmotic pressures on either side of the membrane. Pressure is applied on the saltwater side to overcome the osmotic pressure and force the water through the membrane to the freshwater side of the system, from where it may be recovered. Reverse osmosis is prone to membrane fouling and necessitates high electricity consumption.^[8] These issues become worse for high concentrations of total dissolved solids (TDS). Reverse osmosis is typically used for desalination of water that contains 50 to 50,000 parts per million (ppm) TDS.^[8]

Evaporative methods heat salt water to produce water vapor, which is then condensed and collected as fresh water. The most popular evaporative desalination process is multi-stage flash distillation whereby water is heated to a certain top operating temperature and subjected to a vacuum to flash or evaporate it. The process requires a relatively large heat input in order to bring the water to the flash temperature. Even though advances in technology are helping lower the energy requirement,^[3] evaporative methods are still regarded as energy-intensive and expensive.^[11]

Thus, both membrane and evaporative methods have disadvantages, especially as the water salinity increases above 50,000 ppm. Certain water samples, such as those produced from oil and gas extraction, may contain extremely high TDS levels, often 3-8 times higher than

seawater. This high contamination level renders these waters unfit for reuse or discharge. As membrane methods suffer from increased fouling and pressure requirements, evaporative methods require increased amounts of heat and suffer from scaling as the salinity increases. These additional energy and maintenance requirements serve to greatly increase the overall cost of desalination. Directional solvent extraction has been demonstrated as a low temperature, membrane-free method for desalination and could provide a solution by lowering the energy requirements and maintenance costs.^[3] This paper outlines the development of a continuous process prototype for a directional solvent extraction system, describes possible applications of this technology, specifically for the treatment of “flowback” from shale gas and oil extraction, and suggests design improvements to increase efficiency, optimize component sizes, and decrease energy consumption.

2. BACKGROUND

2.1 DIRECTIONAL SOLVENT EXTRACTION

Directional solvent extraction (DSE) has been demonstrated as a low temperature, membrane free method for desalination of seawater and high TDS water samples such as those encountered in the oil and gas industry.^[3] DSE utilizes the characteristic of certain solvents such as soybean oil decanoic acid, and octanoic acid of dissolving water while themselves being insoluble in water. Furthermore, the directional solvent must not dissolve salts and other contaminants to be effective. These medium chain fatty acids have an aliphatic tail and a carboxylic acid head. The aliphatic tail is a hydrocarbon chain that is hydrophobic, while the carboxylic acid head is hydrophilic. This causes the fatty acids to surround the water molecule and form hydrogen bonds between the polar carboxylic acid head and the water molecule, leaving the salt behind.^[3]

The amount of water that can be absorbed by the solvent depends on the length of the fatty acid chain and the temperature of the solvent. As the length of the hydrocarbon chain increases, the solubility of water in the fatty acid decreases. As the temperature of the mixture increases, the solubility of water in the fatty acid also increases. Decanoic acid can dissolve approximately 38,000 ppm of water at 38 degrees C and 59,000 ppm at 80 degrees C. However, water can only dissolve about 100 ppm of decanoic acid at 25 degrees C. These values show the temperature dependence and directionality of the fatty acid and water mixture.^[3]

Directional Solvent Extraction was developed and demonstrated by Bajpayee et al. and their process is illustrated in Figure 2-1.^[3]

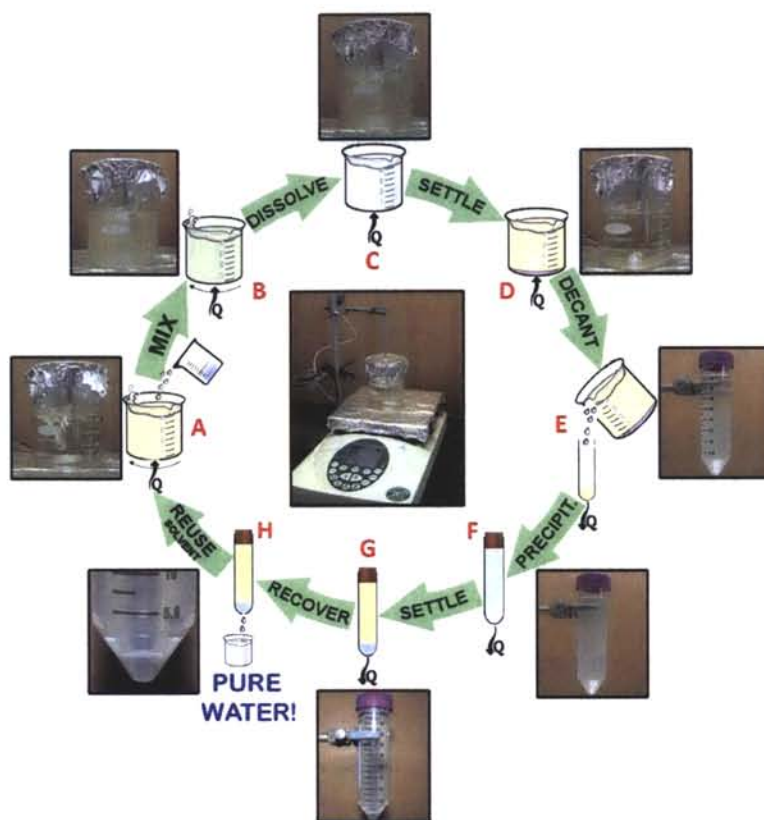


Figure 2-1: An illustration of the basic desalination cycle: (A) decanoic acid is heated and maintained at 40–80 °C and saline solution added while stirring. Upon mixing, (B), the beaker turns cloudy indicating emulsion formation. (C) The cloudiness reduces, indicating dissolution of some water. (D) After stirring is stopped, the remaining brine settles gravitationally, leaving clear decanoic acid with dissolved water above. (E) The clear contents are decanted into a conical tube maintained at 34 °C. (F) The cloudiness reappears as pure water precipitates due to cooling. (G) Pure water separates gravitationally leaving clear decanoic acid above and (H) forming a clear water layer at the bottom. Fresh water is recovered and the decanoic acid reused.

Source: Bajpayee, A., Luo, T., Muto, A., & Chen, G. (2011). Very low temperature membrane-free desalination by directional solvent extraction. *Energy & Environmental Science*, 2011(4), 1672-1675. doi: 10.1039/c1ee01027a

This process was tested as a batch process using beakers and test tubes at the lab bench scale using decanoic acid as the directional solvent. The recovered water was found to have salinity between 700 ppm to 1100 ppm. The World Health Organization (WHO) states that drinking water must contain less than 1000 ppm salt, while the Environmental Protection Agency (EPA) states a 500 ppm salinity limit.³ In addition, an average of only 36 ppm of decanoic acid remained in the final product, which is a negligible amount. This process was proven to work in

these experiments and further market research determined that the technology could be applicable to the challenge of treating produced water from shale oil and gas extraction.^[3]

2.2 SHALE GAS AND SHALE OIL EXTRACTION

The United States Energy Information Administration estimates that there are 750 trillion cubic feet of shale gas and 24 billion barrels of shale oil still recoverable from onshore sites in the lower 48 States.^[13] Exploiting these reserves could reduce America's reliance on foreign oil, which could, in turn, have huge national security, foreign policy, and geopolitical implications. Water challenges, however, are the greatest barriers gating the unhindered development of domestic shale assets.

The advent of hydraulic fracturing has made the extraction of energy from oil and gas shales feasible. Mitchell Energy first used hydraulic fracturing in the 1990's in the Barnett Shale reserves in Texas.^[7] The process involves injecting a pressurized mixture of mostly water and "fracking" chemicals in a viscous gel form into the well to fracture the rocks and release the gas. Sand grains are added to the fracking gel to prop open the fine fissures after the fracturing is completed. The gas seeps through the fractures and into the well bore for extraction. Furthermore, to access a larger deposit area from a single drilling pad, horizontal drilling is used to extend the well horizontally through the layer of shale.^[7] Despite these advances, water related challenges are hindering the development of these assets. Fracturing requires a large amount of water (on average 4.5 million gallons per well), which must be transported in and taken out of the public supply.^[5] In addition, this water gets contaminated with minerals, heavy metals, and organics during the fracturing process and returns to the surface. This contaminated water cannot be discharged or reused without treatment.

The water contains sodium, chlorides, barium, sulfates, oil, iron, heavy metals, and other particulates. The amount of total dissolved solids (TDS) can be extremely high, up to 3-8 times more than that in seawater, which makes conventional water treatment and desalination technologies unfit for use in the application. The high TDS levels result in membrane fouling and undesirable scaling in the treatment systems.^[9] The storage, removal, and approved disposal of shale gas and shale oil "flowback" water is very expensive. It is thus desirable to develop new effective and affordable techniques to treat the "flowback" water and enable continued growth of the shale industry.

As a simple, membrane free process, Directional Solvent Extraction offers a potential method of treating this water in an effective, affordable, and robust manner. Here, we present a continuous Directional Solvent Extraction process that can be applied to the treatment of “flowback”.

3. CONTINUOUS DIRECTIONAL SOLVENT EXTRACTION SYSTEM

3.1 OVERVIEW

In order to make directional solvent extraction a feasible industrial solution, it must be developed into a continuous cycle with a short cycle time and high throughput rates. It must also be as much, or more, economical than the alternative disposal methods, which is mostly transportation to a deep injection well.

Figure 3-1 illustrates a schematic of the continuous process. In the first step the solvent and the feed water are heated. Second, the heated solvent and feed are mixed together. Following this the brine is separated from the solvent-water solution. The fourth step involves cooling the solvent-water solution to precipitate out pure water. The final step separates the precipitated water from the solvent, recovers the fresh water, and returns the solvent to a reservoir for reuse. The solvent runs within the system in a closed loop, the contaminated feed water is the system input, and fresh water is the system output. Ideally, a small amount of waste brine is extracted for disposal. The process is shown schematically below in Figure 3-1.

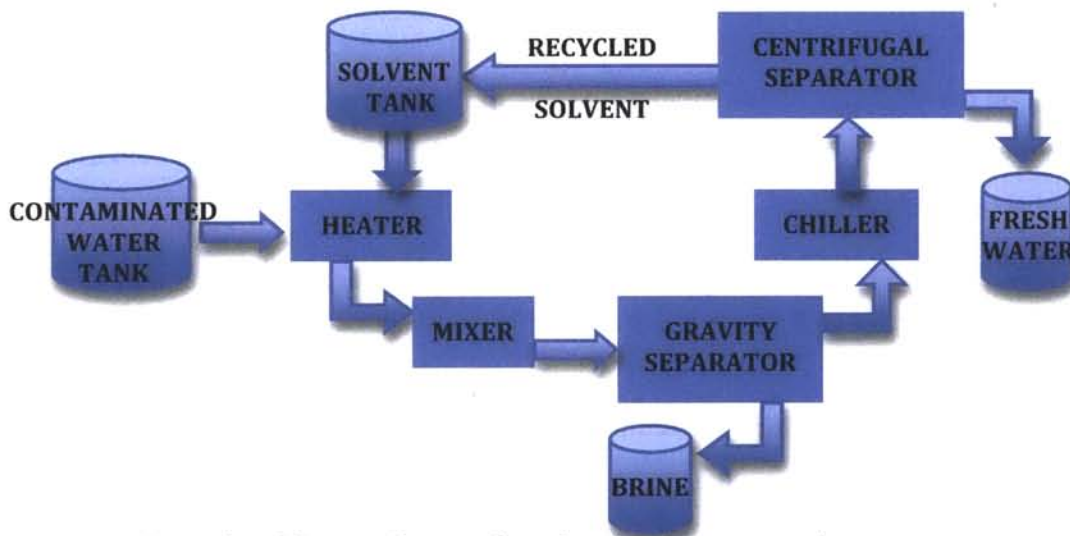


Figure 3-1: Schematic of the continuous directional solvent extraction system. Components of the system include a heater, mixer, gravitational separator, chiller, and centrifugal separator. Contaminated water and solvent enters the heater, brine is extracted in the gravitational separator, fresh water is recovered in the centrifugal separator, and recycled solvent is sent from the centrifugal separator back to the solvent tank.

3.2 SOLVENT SELECTION

The solvent used in this system is octanoic acid [$\text{CH}_3(\text{CH}_2)_6\text{COOH}$]. It has a slightly shorter hydrocarbon chain than decanoic acid [$\text{CH}_3(\text{CH}_2)_8\text{COOH}$], which was used in testing the batch process explained in section 2.1. The shorter chain increases the solubility of water in the solvent. Increasing the solubility serves to increase the fresh water yield per unit volume of the solvent per cycle.

3.3 HEATER

A heater is used, in the first step, to increase the temperature of the solvent and thus the solubility of water in it. Based on Bajpayee's experiments^[3], temperatures between 40 degrees C and 90 degrees C must be maintained in the mixer and the gravitational separator to be able to produce a reasonable amount of fresh water after the separation process.^[2] Heat losses in the mixer and the gravitational separator are inevitable, therefore the higher end of the range given above, 90 degrees C, must be reached in the heaters to ensure that the temperature remains high in the mixer and the gravitational separator. Two resistive flow-through heaters are used to heat both the solvent and the contaminated water before entering the mixer. The heater power is dependent on the flow rate and thermal properties of the fluid passing through it. Flow rates are based on the maximum flow rate of the centrifuge and the ratio of solvent to contaminated water needed to produce fresh water.

The optimal flow rate for the centrifuge used here is 0.07 gallons per minute (GPM) as explained in section 3.7. Based on Bajpayee's report, decanoic acid dissolves 3.8% water at 34 degrees C and 5.9% water at 80 degrees C.^[3] Assuming that octanoic acid will dissolve more water than decanoic acid at the same temperatures, and that the system will be using average high temperatures around 60 degrees C, a ratio of 20 parts solvent to one part contaminated water, 5% water, is used in the system. From this ratio and the flow rate of the centrifuge, the flow rate of the solvent was calculated to be 0.0665 GPM and that of the contaminated feed water to be 0.0035 GPM.

The specific heat capacity of octanoic acid is 2.08 J/g*K and the specific heat capacity of water is 4.18 J/g*K.^[12,14] The change in temperature needed within each heater will be based on the difference between the storage temperature of the solvent and contaminated water, room temperature, and the desired output temperature from the heater, which is 90 degrees C. Using

the specific heat capacities of octanoic acid and water, the flow rates of the two fluids, and a temperature change of 67 degrees C, the power needed to raise the temperature of the fluids to 90 degrees C was calculated. The power needed to heat the solvent is 532 W and the power needed to heat the contaminated water is 62 W. Heat losses caused by inefficiencies in the heater are not accounted for in these calculations.

To account for heat losses and to allow for future scaling of the system to higher flow rates, larger heaters were used. Based on the availability of commercial heaters, a 5000 W heater was implemented into the system to heat the solvent and a 1500 W heater to heat the contaminated water. Both have adjustable settings so that the temperature can be controlled manually. The high power rating allows the system to be scaled up to higher flow rates in the future. Two peristaltic pumps control the flow rates into the heaters and are set to the flow rates for the solvent and contaminated water described above. Figure 3-2 is a picture of one of the heaters during assembly.



Figure 3-2: Liquid flow-through heater used to heat the solvent or the contaminated water before entering the mixer.

3.4 MIXER

After the solvent and contaminated water are pumped through the heater, the fluids enter the mixer at their set flow rates as explained above. The mixer is made up of three parts, a containment vessel, a stirrer, and a stand. The containment vessel is a capped cylinder made from four inch PVC piping. The overall length of the containment vessel is 60 cm. To maintain access to the inside of the containment vessel, the PVC pipe is cut in half and a pipe connector is attached to the inside ends of each half. The pipe can be unscrewed in the middle to gain access to the inside of the containment vessel, and sealed together to prevent leakage of the fluids while

in operation. Gaining access to the inside of the pipe is important for maintenance of the stirrer propeller blade that is described below. Fluids enter and leave the containment vessel through barbed fittings attached to the caps.



Figure 3-3: First iteration of the containment vessel and stand with close up views of the top and bottom caps. The top cap has two ports for the solvent and contaminated water and a hole in the middle for the stirrer rod. The bottom has one port for the output of the mixture to the gravitational separator. The stand uses springs to remove vibrations and allow the PVC piping to expand and contract.

The top cap of the containment vessel has two ports, one for the solvent and one for the contaminated water, and a hole in the middle for the stirrer rod. The bottom cap has one port for the mixture to exit the containment vessel and enter the gravitational separator. A stand holds the containment vessel up using springs to reduce vibrations and allow the PVC to expand and contract with temperature changes. The containment vessel stands vertical and is held a few inches above the ground to allow tubing to enter the exit port at the bottom of the containment vessel. Figure 3-3 shows several views of the first iteration of the containment vessel and stand without the stirrer and before the connector fitting was installed on the containment vessel.

A compact commercial stirrer mixes the solvent and contaminated water in the containment vessel. The stirrer turns a shaft with a three-inch propeller blade attached to the bottom. The stirrer can reach speeds of 2000 revolutions per minute (rpm), and is adjustable by increments of one rpm down to a minimum speed of 40 rpm. The propeller blade is lowered down to the bottom quarter of the containment vessel to ensure that the contaminated water and solvent are properly mixed before exiting. At high speeds the stirrer creates an axial vortex within the containment vessel, which improves the mixing rate, much like a blender. For this system the stirrer is set to 1500 rpm to mix the solvents in an axial vortex. Figure 3-4 shows the final iteration of the mixer. It includes the containment vessel with the pipe connector fitting, the stand, and the stirrer. The heaters are attached to the mixer stand to reduce the footprint of the system and minimize heat losses by shortening the length of tubing connecting the heater to the mixer.

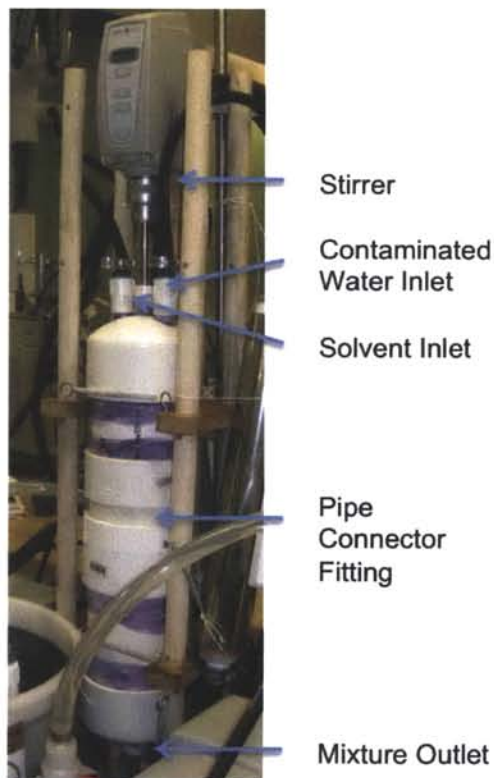


Figure 3-4: Final mixer design. Containment vessel has a pipe connector fitting to allow access to the inside of the pipe for purposes of adjusting the propeller blade of the stirrer. The stirrer turns the propeller blade at 1500 rpm. Solvent and contaminated water enter through fittings on the top cap. The final mixture exits through a fitting on the bottom cap.

3.5 GRAVITATIONAL SEPARATOR

After leaving the mixer, the solvent and contaminated water mixture enters the gravitational separator, where a solution of contaminant and excess water, brine, is extracted for disposal and a solution of water and solvent is extracted for further processing. The height difference between the water level in the mixer and the water level in the gravitational separator causes the mixture from the mixer to flow into the gravitational separator at the same rate as fluids are pumped into the mixer. The goal of the gravitational separator is to separate the brine from the mixture with as little energy input as possible. This design uses gravity and no energy input to separate the mixture relatively quickly. The gravitational separator uses a five-gallon bucket with a horizontal divider to reduce turbulence. Reducing turbulence will reduce the settling time of the two fluids. The walls of the bucket are tapered, which allows a circle with a certain diameter to sit snugly inside at a certain height. The horizontal divider was designed to sit in the bottom third of the bucket and is made out of ABS. Another circular piece of ABS is designed to sit at the very top of the bucket, called the top plate, and provides an attachment site for the inlet and outlet fittings. PVC pipes extend the fittings to specified heights in the bucket, each for a different purpose. Figure 3-5 provides a diagram of the three fittings to supplement the descriptions below.

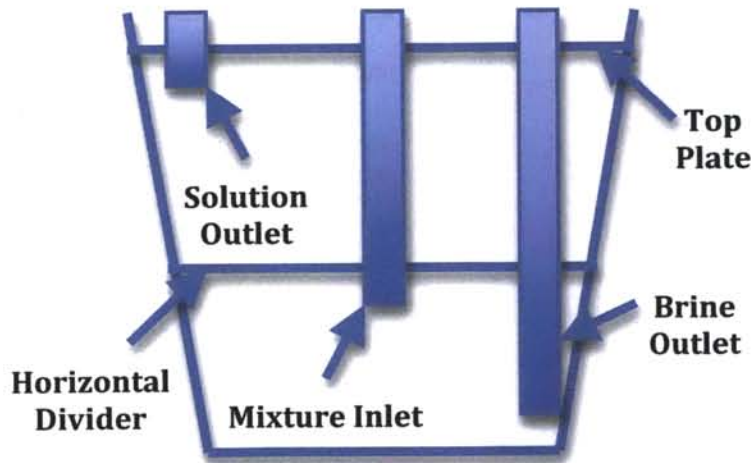


Figure 3-5: The mixture enters in the center of the top plate and a pipe releases the fluid just below the horizontal divider. The horizontal divider reduces turbulence during separation of the input mixture. The lighter solvent and water solution rises to the top and out the solution outlet. The heavier brine sinks to the bottom and is extracted through the brine outlet.

Three barbed fittings on the top plate allow for fluids to enter and leave the gravitational separator. The contaminated water and solvent mixture from the mixer enters the middle fitting, while the solvent and water solution and the brine exit through the two outside fittings. The mixture inlet is connected to a pipe, which runs down the middle of the bucket and extends just below the horizontal divider. The mixture separates into two fluids. The lighter fluid, the solvent and water solution, passes through holes in the horizontal divider and rises to the surface, while the heavier fluid, the brine, sinks to the bottom and is trapped below the horizontal divider. The brine contains any water that was not absorbed by the solvent and any particulates, such as salt, that were carried in the contaminated water.

The brine outlet has a pipe that extends to the very bottom of the bucket. This brine outlet is used to extract the brine periodically to ensure that only the solvent and water solution exists in the upper section of the gravitational separator. To start the flow of brine, air is removed from the piping system at the start of the cycle. A valve allows the flow of brine to be turned on and off. The brine is collected in a waste tank for disposal.

The solution outlet has a pipe that extends just below the top plate. It was originally used to extract the water and solvent solution out of the gravitational separator and deposit it in the chiller in a similar process to that of the brine. However, every time the level of the fluid in the gravitational separator went below the end of the solution outlet pipe, the flow would stop. The brine outlet pipe starts at the bottom of the bucket, and therefore does not have this problem unless the gravitational separator is emptied. In order to restart the flow, air would have to be removed from the piping. To avoid this recurring problem a more direct and reliable method was installed. A hole was cut out of the side of the gravitational separator bucket just below the top plate. The next step in the system, the chiller, also used a five-gallon bucket. A hole was drilled slightly lower than the first in the chiller bucket, and a pipe was attached between the two holes. Gravity now forced the fluid in the gravitational separator to flow into the chiller more reliably than the first design.

The top plate and horizontal divider are connected together by PVC pipes forming an insert that sits inside the gravitational separator bucket. Figure 3-6 shows a picture of this insert, including the outlet pipe that is no longer used in the system. Figure 3-7 shows the final design of the gravitational separator with the insert inside the five-gallon bucket and the outlet pipe extending out from the device.

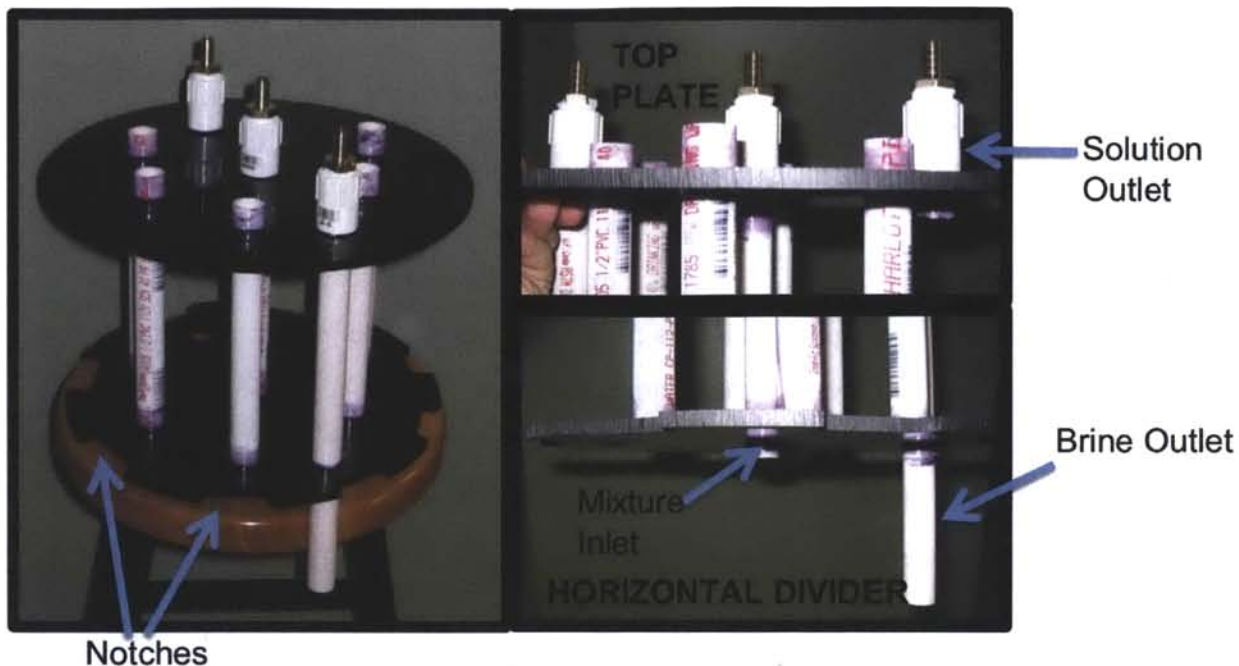


Figure 3-6: The insert for the gravitational separator sits inside a five-gallon bucket. The insert includes a horizontal divider with notches to reduce turbulence and a top plate with barbed fittings to allow fluid to enter and leave the bucket. The inlet pipe extends just below the horizontal divider and carries the mixture from the mixer, the brine outlet pipe extends to the bottom of the bucket and extracts the brine that separates out of the input mixture, and the solution outlet pipe (no longer used) initially extracted the solvent and water solution that separated out of the input mixture.



Figure 3-7: The final design of the gravitational separator with the insert from Figure 7 inside the five-gallon bucket, and the outlet pipe extending out from the top. The mixture from the mixer enters the gravitational separator through flexible tubing, brine is extracted to a waste bucket below the gravitational separator, and the desired solution flows through the outlet pipe and into the chiller without the use of any pumps or input energy.

3.6 CHILLER

The outlet of the gravitational separator contains a solution of solvent and water at a relatively high temperature. When the temperature of the solvent is reduced, the solubility of water in octanoic acid reduces, and the water precipitates out. The precipitated water can then be extracted using a centrifugal separator. The chiller is designed to lower the temperature of the solution from the gravitational separator before it enters the centrifugal separator. The chiller is a simple design that places a stainless steel immersion wort chiller in a five-gallon bucket to chill the solution as shown in Figure 3-8. An immersion wort chiller is made from a long tube of metal wound into a stack of coils as shown in Figure 3-9. Cold water from a chill water source passes through the coils to cool the solution. Water precipitates out and the cooler solution sinks to the bottom of the chiller, where a pump forces the cloudy mixture into the centrifugal separator to recover the fresh water.

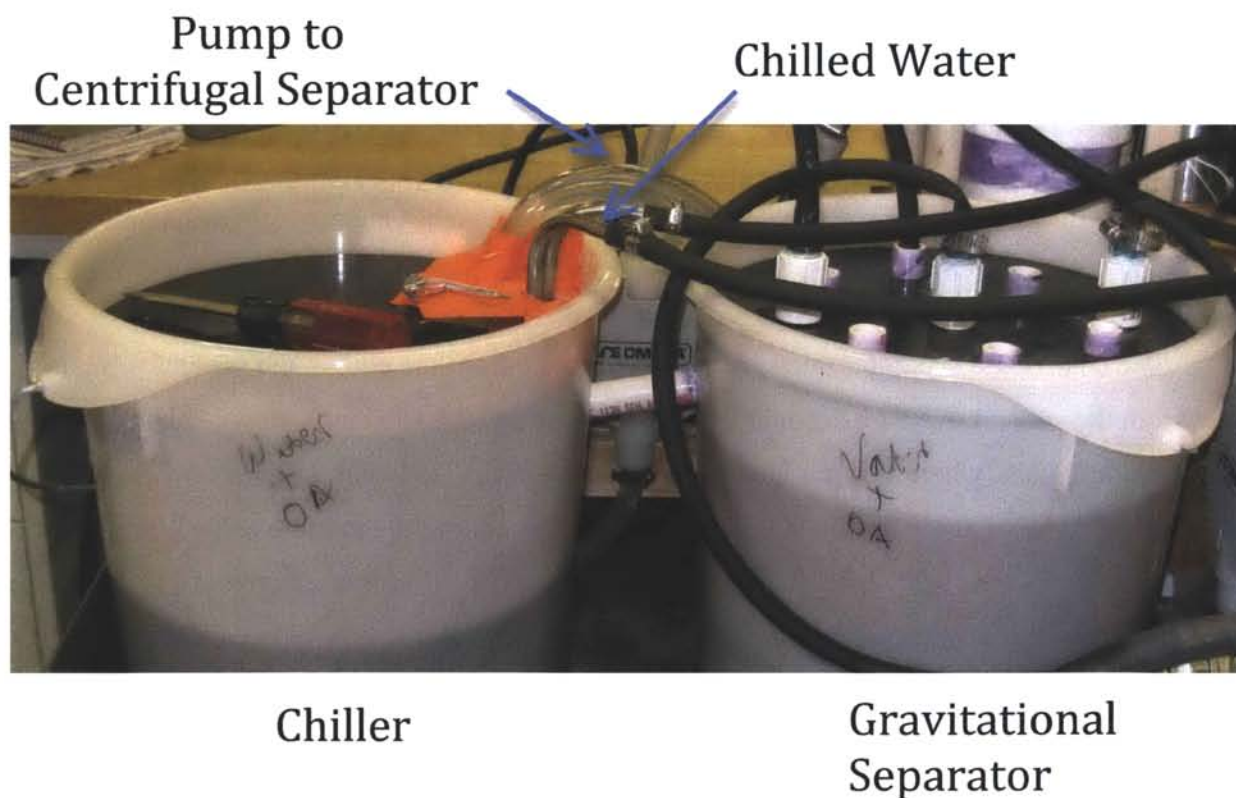


Figure 3-8: An immersion wort chiller sits inside a five-gallon bucket to cool the solvent and water mixture from the gravitational separator. Cooling the solution reduces the solubility of water in the solvent and causes water to precipitate out. A pump extracts the cool solution from the bottom of the chiller to be separated in the centrifugal separator.

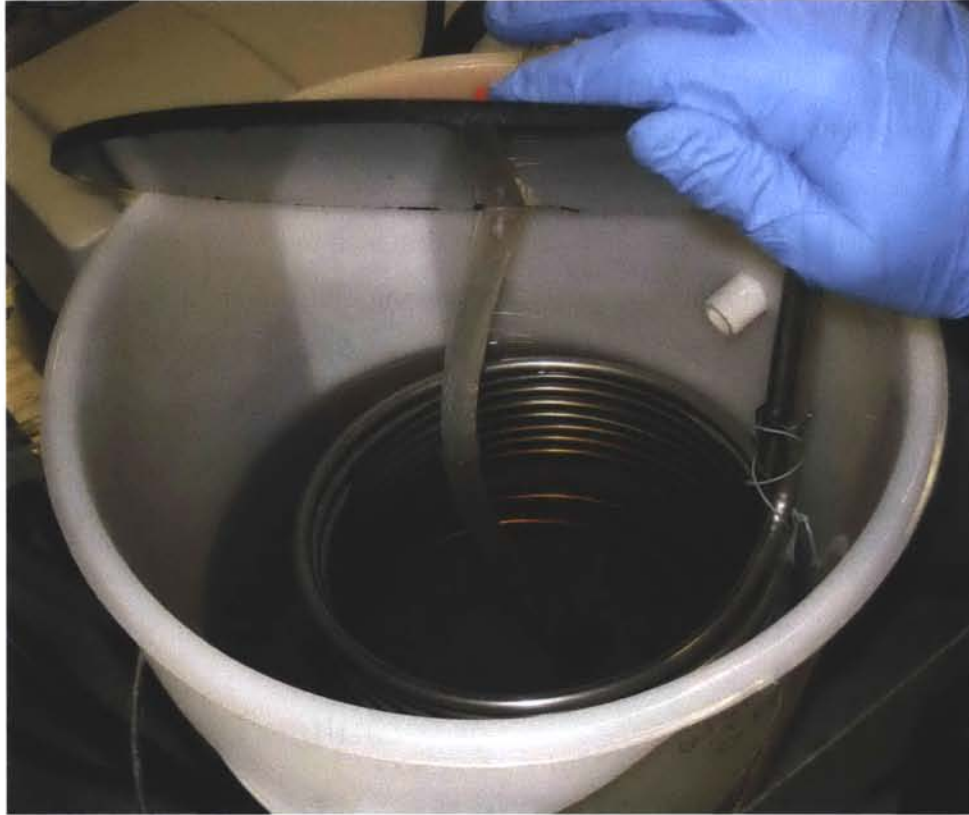


Figure 3-9: This stainless steel immersion wort chiller is used to cool the solvent and water mixture from the gravitational separator before it reaches the centrifugal separator.

3.7 CENTRIFUGAL SEPARATOR

The centrifugal separator takes the cloudy mixture from the chiller and separates fresh water from the solvent. The fresh water is stored for use and the solvent is recycled back into the solvent holding tank, where it is pumped back into the system. In the initial process developed by Bajpayee^[3], the final separation step was completed by setting the mixture aside until the water and solvent separated. After 72 hours, water was collected from the bottom of the test tube at about two percent of the total volume.^[3] Bajpayee also ran the process using a Fisher Scientific Marathon 21000 lab centrifuge, instead of waiting 72 hours, and similar results were found with a 30 second residence time.^[2]

The continuous cycle system uses a CINC Industries model V02 centrifuge to separate the water from the solvent. Fresh water is released through a heavy phase outlet, and solvent is released through a light phase outlet. Using the chart in the CINC centrifuge users manual, shown in Figure 3-10, and given the 30 second residence time from the lab centrifuge test, a flow rate of 0.07 gallons per minute (4.4 mL/sec) was chosen for the continuous system.^[4]

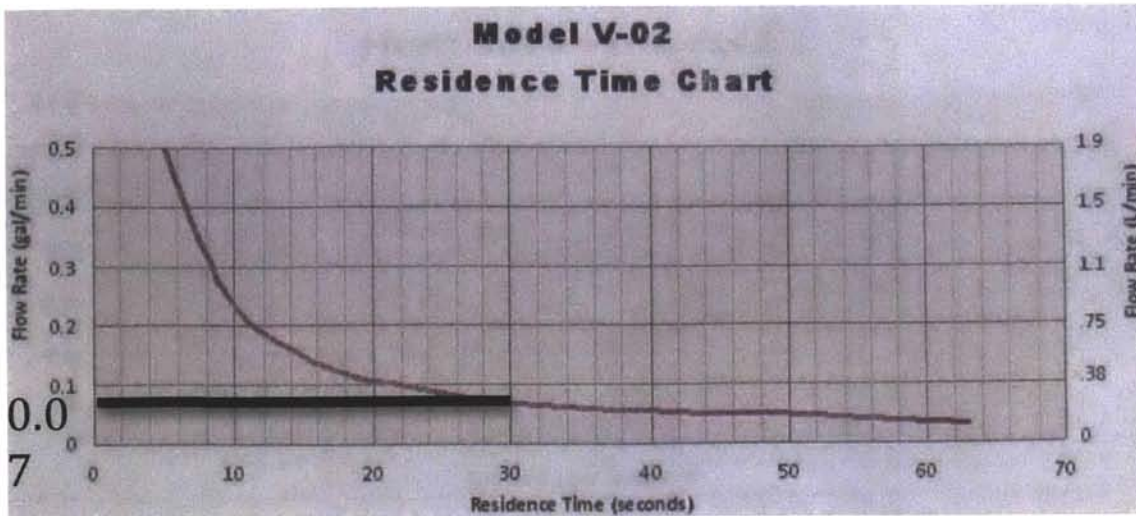


Figure 3-10: Flow rate (gal/min) versus residence time (sec). Given the experimentally determined residence time of 30 seconds, a flow rate of 0.07 gallons per minute is used in the continuous cycle system.

Source: CINC Industries. (2011). *Model V02 operations and maintenance manual*. pg 49.

3.8 CONTINUOUS CYCLE CHARACTERISTICS

The solvent that exits the light side of the centrifugal separator still contains some percentage of water. The amount of water that remains in the solvent depends on the temperature of the solvent as it passes through the centrifugal separator. After the solvent leaves the centrifugal separator it is pumped back up to the heater where the increase in temperature allows it to absorb an additional volume of water. Most of the additional water is later recovered in the centrifugal separator after being cooled in the chiller. The difference between the temperature of the solvent in the gravitational separator and the temperature of the solvent in the centrifugal separator, determines the amount of fresh water that can be produced at a constant flow rate. Increasing this temperature difference will increase the yield of fresh water. However, increasing the flow rate would cause a decrease in residence time of the fluid in the centrifuge, thus reducing the fresh water yield from the system. Figure 3-11 shows the full system setup.

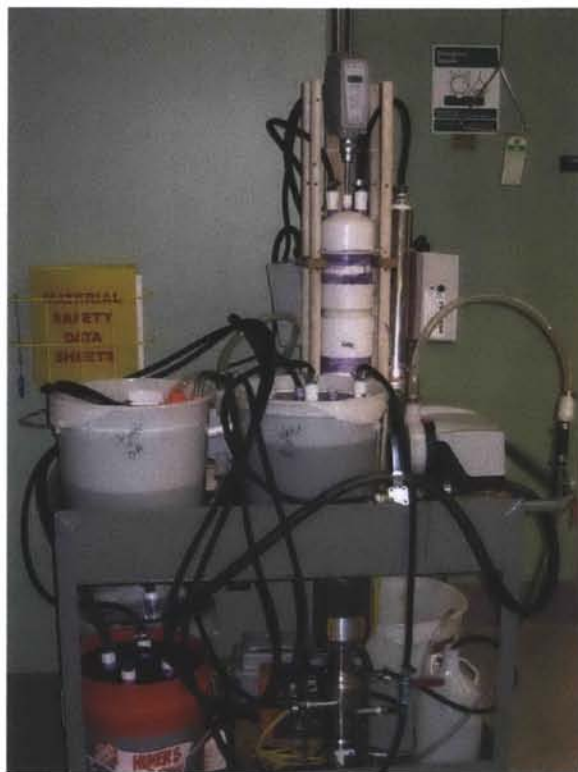


Figure 3-11: Full system setup.

Figure 3-12 shows the change in temperature throughout the system. Samples were taken from different points in the cycle, and the fluids temperature was measured with a thermometer. The change in temperature discussed above is drawn on the figure and marked with a ΔT . The high end of this range was measured from inside the gravitational separator. The low end is measured from the solvent tank. The fluid in the solvent tank is slightly warmer than the fluid that leaves the chiller. This is caused by the work added to the fluid in the centrifugal separator. The increase in temperature in the centrifuge will cause the solvent to reabsorb some of the water. To account for this, the temperature representing the centrifugal separator was taken from the solvent tank and used as the lower bound of the temperature change.

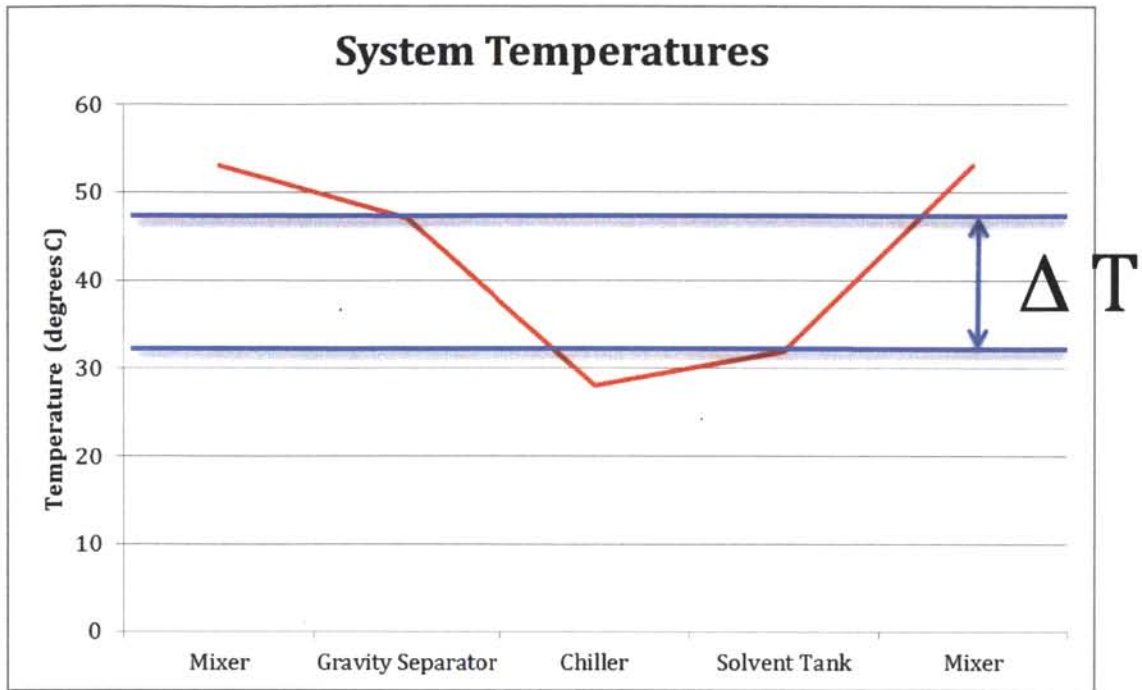


Figure 3-12: Temperature measurements from samples taken at different points in the system. The change in temperature between the gravitational separator and the centrifugal separator scales with the rate of fresh water output.

4. RESULTS

To test whether water could be extracted in a continuous cycle of directional solvent extraction; a test was performed using octanoic acid and pure water. The cycle was run continuously for several hours to allow the solvent to pass through the system multiple times. Samples were taken from the heavy phase output of the centrifuge and tested for water concentration. The first tests showed that essentially no water had been released through the heavy phase output and that the fluid contained mostly solvent. Adjustments were made to the centrifuge, per the instruction manual, to solve the problem of light phase contamination in the heavy phase output. The weir inside the centrifuge, which controls the location of the fluid interface, was replaced. A smaller inner diameter weir moves the fluid interface closer to the center of the rotor and decreases the light phase contamination in the heavy phase output. However, testing of the heavy phase output showed that, again, only solvent was passed through the heavy phase output and no water was found.

To test whether this was a failure of the continuous system or the centrifuge, a sample from the centrifugal separator was centrifuged using a Fisher Scientific Marathon 21000 lab centrifuge at 2000g force for about one minute. This centrifuge was previously used successfully to speed up the solvent and water separation time during testing of the batch process. Processed samples from the lab centrifuge contained about two percent water. This concentration level closely matches those found in experimental tests run by Bajpayee et al with decanoic acid.^[3] This presence of water in the samples showed that the continuous cycle can be used to produce water; however, the CINC centrifuge used in the cycle is not optimized to separate the water from the solvent. The use of centrifuges that are optimized for this system will lead to better results in the future. For all additional tests, samples were passed through the lab centrifuge.

The second set of tests measured the salinity of the fresh water extracted from the samples run through the lab centrifuge. The system was run with octanoic acid and saline water. The input salinity in the contaminated water tank was measured to be 3.5%. This is roughly the concentration of sea water. The system was run for several hours to allow the solvent to recycle back into the system. Samples were taken from the chiller output and passed through the lab centrifuge. About one percent of the mixture was observed to separate out as water. The water was extracted and its salinity was measured using an Atago salt meter. The average sample

contained 1750 ppm salt (0.175%), with the best sample containing zero salt. This is only slightly above the range of the WHO and EPA drinking water standards and within the range of reuse standards for oil and gas operations.

5. IMPROVEMENTS

The lack of water produced by the CINC centrifuge continued after repeated attempts to adjust the location of the fluid interface to reduce light phase (solvent) contamination in the heavy phase (water) output. A likely cause of the contamination is that the residence time was too low. Increasing the residence time would improve the separation of the water from the solvent. However, increasing the residence time would require decreasing the flow rate of the system, and that would decrease the fresh water yield. A more powerful centrifuge capable of handling a higher flow rate and optimized for the expected ratio of the centrifuge outputs, solvent and water, will provide better results. This was substantiated by the effective use of the lab centrifuge.

A second improvement focuses on maintaining a high temperature difference between the gravitational separator and the centrifugal separator. Adding insulation to the mixer containment vessel and the outside of the gravitational separator will reduce the heat lost to the environment, thus raising the temperature in the gravitational separator.

Another recommended improvement is to combine the mixer and gravitational separator by placing the mixer inside the gravitational separator. This will reduce the length of flexible tubing between the mixer and the gravitational separator, thus reducing heat losses and increasing the temperature in the gravitational separator. This will also decrease the footprint of the system and simplify the process.

6. BASIC COST ANALYSIS

The majority of the energy goes into heating the fluids. The heaters are a necessary component of the system. The difference in temperature between the gravitational separator and the centrifugal separator scales with the flow rate of fresh water out of the system. The power drawn by the two heaters totals 6500 W. The centrifugal separator has the next largest power demand at just 100 W. The pumps and mixer require less than 50 W of energy each. The peristaltic pumps and stirrer use motors that require about 50 W electricity. The total power needed to run the system is 6770 W. At a solvent to contaminated water ratio of 20 to 1 and system flow rate of 4.4 mL/sec, the contaminated water flow rate is 0.19 mL/sec. At this flow rate, the energy needed to process one barrel (42 gallons) of contaminated water is 135 MJ. At average electricity costs in the United States, \$0.12 per kWh^[6], this translates to a cost of \$4.50/bbl. Assuming two percent fresh water is recovered from the system, with a system flow rate of 4.4 mL/sec the flow rate of fresh water out of the system is 0.09 mL/sec. In this case the energy required to produce one barrel of fresh water is 285 MJ of electricity, which would cost \$9.50/bbl in the United States. By using a 1500 W heater to heat the solvent, rather than the 5000 W heater, the price to process one barrel of contaminated would drop to \$2.17/bbl and the cost to produce one barrel of fresh water would drop to \$4.59/ bbl. Companies such as Fountain Quail Water Management and Purestream Technologies use some form of the evaporative method of water purification described in the background section of this report to process flowback water from shale gas and shale oil extraction. These processes have operational costs of about \$5/bbl of flowback water.^[1,10] The lab prototype continuous cycle using directional solvent extraction described in this paper costs about \$4.50/ bbl in energy input. In a field prototype most of this energy would come from natural gas fuel, and thus cost less than grid electric power. This calculation does not account for the capital costs of the system, which in this case were about \$10,000. At a prototype-level these operational cost estimates are extremely encouraging and suggest that this process could potentially provide an effective, affordable method of treating flowback water and other high contamination water samples.

7. CONCLUSION

Directional solvent extraction promises to be a simple, effective, low cost water treatment process. A prototype of a continuous directional solvent extraction process was built and tested. The system was shown to produce about 2.5 gallons of water per day with an energy consumption of 6.7 kW. It is expected that the maximum capacity of this particular system is about 7 GPD. Improvements in the design to increase efficiency and optimize each component will decrease the systems energy demand and increase fresh water throughput. There are many potential uses of this system, including production of fresh water from seawater and treatment of high TDS flowback water from shale gas and shale oil extraction. Commercialization of this process could help enable the United States to continue to develop its domestic fossil fuel assets and significantly reduce its dependence on foreign oil. This could have profound impacts on United States' foreign policy and defense strategy as well as on world geopolitics.

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