Spring 2012

Total Organic Carbon Rejection in Osmotic Distillation

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Recommended Citation

Shaw, Hali Laraelizabeth, "Total Organic Carbon Rejection in Osmotic Distillation" (2012). *Master's Theses*. 4172.
DOI: https://doi.org/10.31979/etd.tnqh-e6ak
https://scholarworks.sjsu.edu/etd_theses/4172

TOTAL ORGANIC CARBON REJECTION IN OSMOTIC DISTILLATION

A Thesis

Presented to

The Faculty of the Department of Biomedical, Chemical and Materials Engineering

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Hali Laraelizabeth Shaw

May 2012

The Designated Thesis Committee Approves the Thesis Titled

TOTAL ORGANIC CARBON REJECTION IN OSMOTIC DISTILLATION

by

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APPROVED FOR THE DEPARTMENT OF CHEMICAL AND MATERIALS ENGINEERING

SAN JOSÉ STATE UNIVERSITY

May 2012

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ABSTRACT

TOTAL ORGANIC CARBON REJECTION IN OSMOTIC DISTILLATION

by Hali L. Shaw

The osmotic distillation (OD) system is a spacecraft wastewater recycling system designed to produce potable water from human urine and humidity condensate. The OD system uses vapor-liquid separation to purify the wastewater across an osmotic distillation membrane, which is microporous and hydrophobic. When treating a mixture of urine and humidity condensate, the OD can produce water with a non-purgeable total organic carbon (NPTOC) concentration of less than 7 ppm; however, it is unclear what mechanism allows the system to achieve such a high total organic carbon (TOC) rejection when compared to other conventional distillation-based water treatment systems.

The hypothesis for this study was that osmotic agent concentration and feed pH influence TOC rejection in osmotic distillation. The objective of this research was to determine the effect of the ionic strength of the osmotic agent and the pH of the feed solution on TOC rejection. The feed pH values studied included 3, 7, and 10, and the osmotic agent concentrations studied were 20, 30, and 40 g/L (NaCl in water). The results of this research clearly indicated that feed pH had an effect on NPTOC rejection in osmotic distillation. The pH 3 treatments resulted in significantly higher TOC concentrations in the osmotic agent when compared to the feed pH values of 7 and 10. Based on statistical analysis, the osmotic agent concentration did not have an effect on TOC rejection in osmotic distillation.

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CHAPTER ONE
INTRODUCTION

The osmotic distillation (OD) system is a membrane-based water treatment process proposed to produce potable water from human urine and humidity condensate. The technology can be used for long duration human space flight missions, or it can function as an emergency spacecraft backup treatment system. The OD system has been tested extensively at NASA Ames Research Center for the recycling of urine and humidity condensate into potable water. This system can also be used to separate a wide range of solvent-solute mixtures with different boiling points. The process consists of two stages starting with OD, which is then followed by reverse osmosis (RO), as shown in Figure 1. Osmotic distillation uses vapor-liquid separation to purify the wastewater across an osmotic distillation membrane, which is microporous and hydrophobic.

The driving force for mass transfer to occur across the OD membrane is a concentration gradient resulting in a vapor pressure differential. Based on membrane design (surface tension, contact angle, capillary pressure, and pore radius), only volatile components or vapor can pass through the pores of the membrane. The liquid phases have a high enough surface tension that a meniscus forms across the pore inlet and outlet. At nearly room temperature, the primary volatile in the higher vapor pressure solution (feed) evaporates, passes through the membrane pores as vapor, and condenses into the lower vapor pressure solution (osmotic agent). The feed or influent wastewater consists of a urine and humidity condensate mixture that is formulated based on the characteristics of transit mission wastewater on spacecraft [1]. The receiving solution on the pressure side of the membrane, or the osmotic agent (OA), is a salt-water (NaCl) solution. The two liquid streams recirculate counter-currently under ambient conditions. When treating a mixture of human urine and simulated humidity condensate, the feed was observed to have an initial non-purgeable total organic carbon (NPTOC) value between 1400 to 1700 ppm [2]. The OD can produce water with a NPTOC concentration of less than 7 ppm, although it is unclear as to what mechanism allows the system to achieve such a high total organic carbon (TOC) rejection when compared to other conventional distillation-based water treatment processes. When treating similar feed compositions, these distillation systems typically produce water with TOC concentrations ranging from 20 to 300 ppm, which is significantly higher than the product water produced by the OD system [2,3].

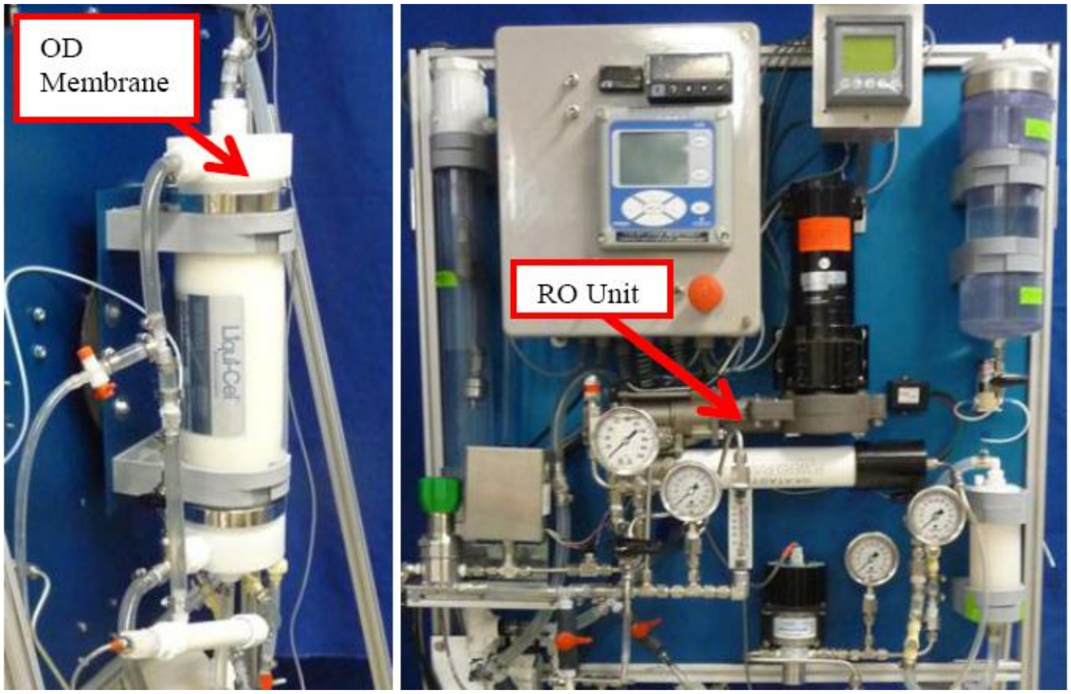

Figure 1. OD system components.

Previous tests have indicated that there is a relationship between TOC rejection and ionic strength [2]. It was hypothesized that when increasing the concentration of the OA, the OD achieved an increase in TOC rejection. Numerous factors may play a role in total organic carbon rejection, including solubility of contaminants, water activity, concentration polarization, temperature polarization, viscosity, pH, operating pressure, operating temperature, and membrane design [4–19]. The hypothesis studied in this thesis was that osmotic agent concentration and pH of the feed influence TOC rejection in osmotic distillation. The pH of the feed is particularly important because NASA is considering changing the standard feed pretreatment approach as well as proposing raising the feed pH. The objective of this study was to determine the effect of the osmotic agent and pH of the feed solution on TOC rejection. This resulted in future design considerations and identified the governing parameters of the osmotic distillation system.

1.1 Significance

The cost to bring water into space is extremely high. In 2003, the estimated cost to launch the Space Shuttle to Low-Earth Orbit (LEO) was roughly $25,000 per kilogram [20,21]. Although the precise value is not known and will vary for future vehicles, this approximate cost of $25,000/kg was used as a benchmark for this study. The OD system was designed specifically to reduce this expenditure by recycling urine and humidity condensate into potable water. The technology can be used for short duration space missions, or can function as an emergency spacecraft backup treatment system. The system may additionally be considered for long duration space missions since the performance of the system has exceeded expectations.

The OD system was originally projected to last for approximately 336 hours. In previous tests, the lifespan of the system exceeded 1000 hours [2]. The osmotic distillation system can achieve 80% water recovery and is potentially low in mass (8 kg/person), power (approximately 20 W·hr/L), and volume (0.024 m^3/person). The reason that system is still considered to be in a research phase (rather than deployed) is that the technology is not completely understood. Using the osmotic distillation system to produce potable water from spacecraft wastewater is a unique application. Understanding the governing parameters in osmotic distillation is imperative for future design, and research is necessary to advance the technology to a level where it is suitable for human use in space.

CHAPTER TWO
BACKGROUND

The OD system separates an aqueous solution by using a hydrophobic, micro-porous membrane. The term osmotic distillation is rather a misnomer because the liquid feed is not at its boiling point; this process occurs due to evaporation that occurs at ambient temperature and pressure. The driving force for OD is the difference in vapor pressure between the liquid feed solution (a mixture of urine and humidity condensate) and the osmotic agent solution (NaCl in water). Based on the design of the membrane, the surface tension of each contacting liquid is high enough so that a meniscus forms across the inlet or outlet of the membrane pores. Only volatile feed components or vapor can pass through the pores of the membrane [5]. The liquid phases will not pass through the membrane as long as the capillary pressure has not been exceeded.

In OD, the water vapor from the feed evaporates across a meniscus at the pore inlet, as shown in Figure 2. The water vapor is able to travel though the pore of the membrane by either diffusion or convection [5]. Once the vapor reaches the pore outlet, the vapor condenses across the meniscus into the OA; this dilutes the osmotic agent solution. The ionic strength of the OA must be significantly higher than the feed solution in order to maintain an osmotic vapor pressure potential across the membrane. As the ionic strength between the two solutions approach equilibrium, the flux decreases until water is no longer produced. Over time, as water is removed from the feed, the concentration of contaminants in the feed increases. This increase in concentration causes an increase in the osmotic potential (or pressure) of the feed, which leads to a decline in flux.

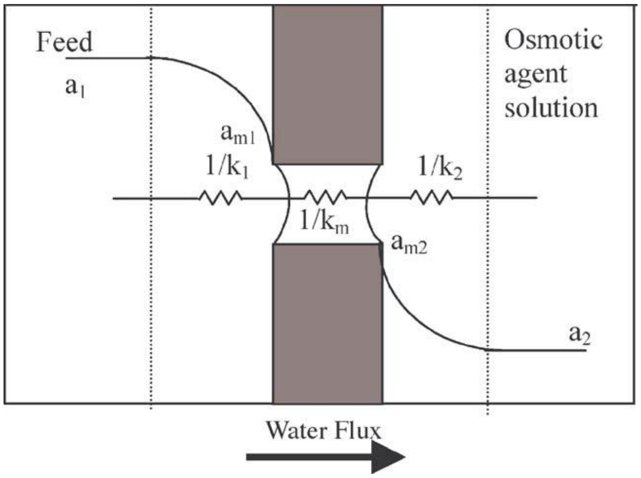

Figure 2. Osmotic distillation mechanism: water activity profile and mass transfer resistances [10]. (Reprinted with permission from Elsevier.)

As the water in the feed solution evaporates, the solution is cooled by absorbs the latent heat of vaporization. Furthermore, as water vapor condenses into the OA, the osmotic agent is heated by releasing the latent heat [5]. The resulting temperature differential is in the opposite direction of the driving force, which will reduce and ultimately stop mass transfer. In order to prevent this issue from occurring, osmotic distillation membranes must be thin and have a high thermal conductivity. Heat then transfers back across the membrane at a high rate through conduction [5]. Due to the rate of heat transfer and by maintaining a thermal equilibrium across the membrane, osmotic distillation is considered essentially isothermal.

In osmotic distillation, the water availability or water activity of the feed and the osmotic agent solution was hypothesized to effect TOC rejection. Water activity is a conceptual dimensionless parameter. It is defined as the ratio between the vapor pressure of water above the solution and the vapor pressure above pure water at a constant temperature. Activity is determined by surface interactions and capillary forces as well as colligative effects of soluble components that interact with water through hydrogen bonds, dipole-dipole interactions, and ionic bonds. In OD, the concentration of non-water contaminants in the feed increases as water is continuously removed, causing the water activity to decrease. As the activity of water decreases, the amount of energy or the latent heat of vaporization required for the evaporation of water increases resulting in a reduced driving force. Water activity and TOC rejection may be influenced by the pH of the feed and the ionic strength of the osmotic agent. The ionic strength of the osmotic agent solution may have an impact on the vapor liquid equilibrium or the solubility of semi-volatile and volatile organics in the OA or TOC rejection. NaCl has low water solubility and a lower water activity than pure water [5]. As the concentration of NaCl in water increases, the surface tension of the solution increases and the vapor pressure of the water decreases. As a result, the water activity of the solution decreases, which could have an effect on the TOC rejection of the membrane. Similarly, it was also hypothesized that pH has an effect on water activity. Changing the pH has been shown to determine whether a compound is in molecular or ionic form, which may influence water activity [22].

In addition to water activity, several additional factors may affect TOC rejection including the surface charge of the membrane. The surface charge of a membrane has been shown to influence membrane rejection performance in electrodialysis and reverse osmosis [23–25]. The surface charge is dependent upon the isoelectric point of the membrane surface and the pH of the contacting solution [23].

Another factor that may affect total organic carbon rejection is concentration polarization. Concentration polarization in osmotic distillation occurs when boundary layers of concentrated feed form on the membrane surface. Conversely, the concentration of the osmotic agent on the surface of the membrane is lower than in the bulk solution due to the direction of mass transfer across the membrane. The boundary layers along the two sides of the membrane can decrease the osmotic potential between the feed and the osmotic agent [6]. A decrease in the osmotic potential difference across the membrane leads to a reduction in the driving force and thus the flux rate of the process. In addition to flux, concentration polarization may influence TOC rejection. The formation of boundary layers, or the concentration gradient on the membrane surface, may influence the amount of semi-volatile constituents that are able to pass through the membrane pores. A lower concentration of organics along the surface of the membrane may result in an increase in TOC rejection.

Temperature and temperature polarization may also have an important effect on TOC rejection. Temperature polarization occurs when the temperatures between the surfaces of the membrane and their bulk solutions vary. Temperature polarization occurs because of the evaporation and condensation of water, which takes place at the pore inlet and outlet [6]. Temperature polarization or thermal gradients may influence TOC rejection in osmotic distillation. Based on Henry’s law, the vapor-liquid equilibrium or the solubility of a gas in a liquid is dependent upon the pressure of that gas at a specific temperature. As a result, changes in temperature may influence the solubility of semi-volatile components in the feed, which may affect TOC rejection.

Although there are numerous factors that may affect TOC rejection, the hypothesis in this study was that osmotic agent concentration and feed pH affect TOC rejection in osmotic distillation. Several equations may relate water activity to TOC rejection. Equation 1 is Henry's Law, which may be used for determining the amount of semi-volatile and volatile organics that are soluble in a solution. Henry's Law states that the partial pressure of a gas is directly proportional to the concentration of the component in solution multiplied by Henry's constant,

$$p_A = x_A H_A(T) \qquad \text{Equation 1}$$

where p_A is the partial pressure of solute A, x_A is the concentration of the solute, and H_A is Henry's constant, which is temperature dependent.

Equations 2–4 were developed by Tromans for determining the solubility of oxygen into inorganic solutes [4]. Equations 2 and 3 are used for determining the ratio between the apparent partial molar volume of the component (V_{app}) divided by the partial molar volume of pure water.

$$V_{app} = \left\{\left(\frac{1000 + C_I M_I}{d_s}\right) - C_I V_I\right\} \cdot \frac{M_{H_2o}}{1000} \qquad \text{Equation 2}$$

$$V_{H_2O} = \frac{M_{H_2O}}{d_{H_2O}} \qquad \text{Equation 3}$$

C is the molar concentration, *M* is the molecular weight, *V* is the molar volume, and *d* is the density for either the inorganic electrolyte (*I*) or water.

Equation 4 was developed to represent the relationship for the solubility of oxygen in inorganic solutes:

$$\left(c_{aq}\right)_I = \phi c_{aq} = \phi P_{O_2} k \qquad \text{Equation 4}$$

where $\left(c_{aq}\right)_I$ is the molar concentration in the presence of ions (*I*), ϕ is the fractional amount of water that is available to dissolve oxygen, c_{aq} is the solubility of oxygen in pure water, P_{O_2} is the partial pressure of oxygen, and *k* is the equilibrium constant [4].

Equation 5 was developed for calculating the driving force across osmotic distillation membranes [6]. Based on this equation, the driving force is determined by the relationship:

$$\Delta\Pi = \Delta \mathrm{p} = \mathrm{p}_\mathrm{F}^0 \mathrm{a}_1 - \mathrm{p}_\mathrm{D}^0 \mathrm{a}_2 \qquad \text{Equation 5}$$

where $\Delta\Pi$ is the osmotic potential, p^0 is the saturated vapor pressure (of the feed F and distillate D), a_1 is the liquid activity of the feed, and a_2 is the liquid activity of the osmotic agent.

Equation 6 is the general equation used for determining the activity of *a* species *i*,

$$a_i = \frac{f_i(\mathrm{T}, \mathrm{P}\{x\})}{f_i^0(\mathrm{T}, \mathrm{P}_i^0)} \qquad \text{Equation 6}$$

where f_i is the fugacity of species *i* with respect to a constant temperature T, pressure P, and concentration *x*, and f_i^0 is the standard fugacity with respect to temperature at some standard pressure P_i^0.

2.1 Primary Outcome

The main objective of this work was to determine whether the ionic strength and feed pH are the major governing factors in OD osmotic agent TOC levels. This resulted in future design considerations and identified the governing parameters of the osmotic distillation system.

CHAPTER THREE
LITERATURE REVIEW

Osmotic distillation has been used in a variety of applications including the concentrating of fruit juice [26]. The OD system used in this study was designed specifically to produce potable water from human urine and humidity condensate. A similar technology developed for solvent recovery does exist and has been patented [27,28], although using osmotic distillation specifically for the reclamation of spacecraft wastewater is a unique application. Unlike the OD system used in this study, the goal in most osmotic membrane distillation processes is to obtain high quality concentrate or feed rather than pure extracted water. This aspect is what distinguishes this osmotic distillation system from others.

Previous osmotic distillation studies have been conducted on the effects of parameters such as flow rates, temperature, concentration, polarization, as well as heat and mass transfer modeling [6–8,10–17,29]. Studies have also been done on the membranes used in OD, including the effect of pore size, liquid penetration, surface tension, and membrane geometry [8–10]. The influence of ionic strength or concentration of the osmotic agent (OA) has been studied as well although the primary outcome of this research was in terms of flux rates rather than rejection of contaminants [26]. Therefore, the objective of this study was to determine the effect of the ionic strength of the osmotic agent and pH of the feed solution on total organic carbon rejection in osmotic distillation.

3.1 Study Related to Testing of the Hypothesis

3.1.1 Study related to Water Activity

Previous testing of the osmotic distillation system used in this study showed that an increase in osmotic agent concentration resulted in an increase in TOC rejection of the membrane [2]. Although these studies were not statistically valid sets of data, this relationship was thought to be due to water activity and the solubility of semi-volatiles. Additionally, a correlation was believed to exist between the previous observations of the OD system and the research conducted by Tromans. Tromans developed a model specifically for predicting oxygen solubility in water and electrolyte solutions based on thermodynamic analysis, as shown in Equation 7 [4].

$$(\mathrm{c}_{\mathrm{aq}})_{\mathrm{I}}/P_{\mathrm{O}_2} = k\phi_{\mathrm{eff}} \qquad \text{Equation 7}$$

The difference between Tromans' study and this study is the use of a semi-permeable membrane as well as heterogeneous volatile and semi-volatile components. Tromans based his model on the concept that the spacing between ions and water molecules should be influenced by molecular perturbations and interactions. The apparent partial molar volume of the ionic components (V_{app}) takes into account the effect of molecular interactions on the spacing between water molecules, which is different from pure water [4]. The results showed that the apparent volume V_{app}, decreases as the ionic solute concentration increases. Tromans also developed correlations between temperature, viscosity, and solubility. The model developed by Tromans estimates the solubility or molar concentration of oxygen in electrolyte solutions at various temperatures and partial pressures of oxygen. This model provided values in agreement with data that has been published [4]. Based on Tromans' research, as the inorganic solute concentration increased, the solubility of oxygen in the liquid decreased. A relation was believed to exist between Tromans' work on water activity and the effect of osmotic agent concentration on TOC rejection in osmotic distillation.

3.2 Studies Related to Hypothesis Development

3.2.1 Studies Related to Effect of pH

The pH of the feed was thought to have an effect on TOC rejection in osmotic distillation due to water activity, surface tension, and surface charge. Most human urine consists of approximately 95% w/v water, 2.5% w/v urea, and 2.5% w/v inorganic salts. These values are not exact because the composition of urine varies greatly and is dependent upon food and liquid consumption, exercise, and many other factors [31]. Transit mission wastewater roughly consists of 33.4% v/v human urine, 46.3% v/v humidity condensate, and 9.1% v/v urine flush water [1]. Changing the pH of this feed mixture is essentially like adding salt or ions to the solution. The addition of salt or the process of salting out has been used in protein purification and has also been used to separate organic compounds from water. By adding salt to a solution, the amount of water that is available to the solute is reduced, which causes the organic phase to separate from the aqueous phase [32]. In addition to salting out, changing the pH determines whether a compound is in molecular or ionic form. Specific classes of compounds with pK_a values of less than approximately 7–9 (such as alcohols, phenols, and carboxylic acids) dissociate to a significant degree in water [22]. As a result, changing the feed pH may influence whether a compound is volatile, which may affect TOC rejection in osmotic distillation.

The pH of the feed may also influence the surface tension of the contacting liquids, which may play a role in TOC rejection. The surface tension of the membrane and the liquids in contact with the membrane surface are important factors in osmotic distillation. The osmotic distillation membrane is hydrophobic, which means that liquids are not allowed to pass through the pores of the membrane [5]. The surface tension of the contacting liquids influence how far the liquid streams are able to penetrate within a membrane pore. Adding salt to water increases the surface tension of the solution. Conversely, adding soap to water lowers the surface tension of the solution. Adjusting the pH of a solution by adding acid or base is similar to adding salt to water. Therefore, adjusting the pH of the feed may affect the surface tension of the solution and resultantly TOC rejection. Weissenborn *et al.*, 1996, studied the surface tension of aqueous solutions containing electrolytes [33]. The research focused on the relationship with ion hydration, oxygen solubility, and bubble coalescence [33]. The results from the study showed that the greatest surface tension increase was caused by highly hydrated anions and cations. The anion-cation pairing is what determines whether the surface tension actually changes [33]. Multivalent electrolytes also had a greater effect on surface tension than 1:1 electrolytes, as shown in Figure 3. Figure 3 shows the effect of the electrolyte activity on the change in surface tension; activity represents concentration and was used to thermodynamically compare 1:1 electrolytes and multivalent electrolytes [33]. Weissenborn *et al.* also determined that water structure, which correlates to surface tension, might be indirectly measured by viscosity and ion hydration [33]. The results of the study in relation to osmotic distillation show that different electrolytes show different changes in surface tensions with respect to concentration. Therefore, adding acid or base to a solution may have a significant impact on surface tension and possibly TOC rejection.

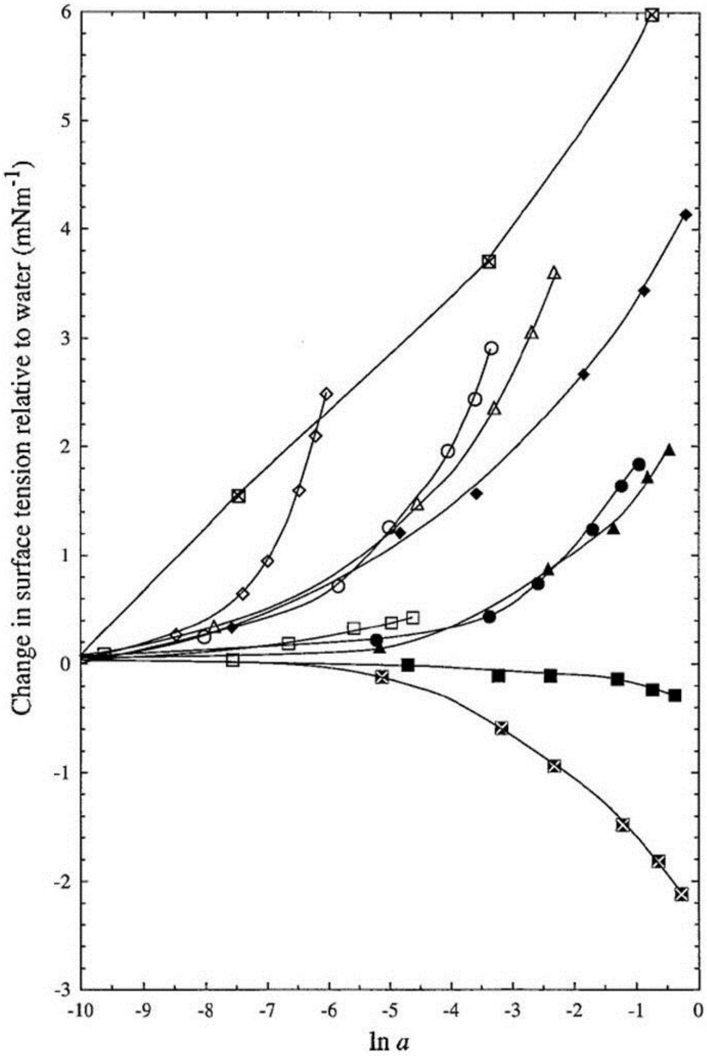

Figure 3. Effect of electrolyte activity (as ln *a*) on the change in surface tension relative to water (Δγ). HCl (■) , LiCl (▲) , KCl (●) , $MgCl_2$ (♦) , $LaCl_3$ (☒) , H_2SO_4 (□), Li_2SO_4 (Δ), Na_2SO_4 (○), $MgSO_4$ (◇) , and $HClO_4$ (☒) [33]. (Reprinted with permission from Elsevier.)

In electrodialysis and reverse osmosis (RO), the surface charge of the membrane has been shown to influence membrane rejection performance [23–25]. Membrane surface charge is dependent upon the pH of the contacting solution and the isoelectric point of the membrane. Qin *et al.*, 2004, studied the relationship between feed pH and permeate pH in reverse osmosis using municipal water as the feed [23]. In this study three different RO membranes named X-20 (neutral surface charge), ESPA1 (high surface charge), LFC1 (low surface charge) were tested with varying isoelectric points of 3.2, 3.6, and 6.5 respectively. The results of the study showed that at a certain pH value the ion rejection (Na^+ and Cl^-) increased with decreasing surface charge (ESPA1, X-20, LFC1), as shown in Figure 4. Based on this study feed pH has an important influence on membrane characteristics, the separation of ions [23], and therefore possibly TOC rejection.

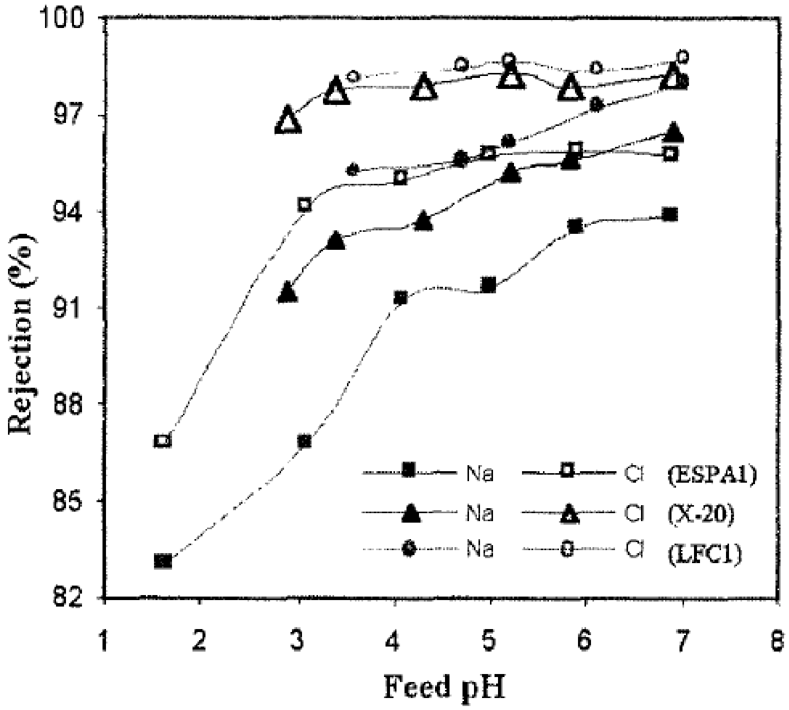

Figure 4. Feed pH versus individual ion rejection for reverse osmosis membranes using municipal water feed [23]. (Reprinted with permission from Elsevier.)

3.2.2 Osmotic Agent

In order to achieve higher flux rates in osmotic distillation, the effect of using various osmotic agent (OA) solutions has been studied [5,26,34]. The optimal osmotic agent should be thermally stable as well as low cost, nontoxic, noncorrosive, and not cause scaling or fouling of the membrane [5]. The osmotic agent should also be a nonvolatile solute that has a high surface tension and a high osmotic activity (i.e., a low vapor pressure, which results from using a solute with high water solubility and low equivalent weight) [5]. Molecule size is an important factor in choosing an OA; as the size of the molecules decrease, more molecules are able to dissolve into the solution. As the concentration of ions in the OA increases, the driving force or the osmotic potential increases. Several other extraction solutions may be used although the most common are NaCl and $CaCl_2$ [5,26].

Celere *et al.*, 2003, studied various osmotic agents and their effects on water flux rates as well as other mass transfer effects on the osmotic distillation process [26]. The osmotic agents tested included $CaCl_2$, propylene glycol (PG), glycerol, and glycerol salt mixtures. Vapor-liquid equilibrium experiments were conducted between an osmotic agent and a detector liquid in order to determine the water activity of the OA solutions [26]. A refractometer was used to measure the concentration of the solutions 5–7 days after the start of each experiment. The results showed that the refractive index or concentration was very similar for all of the osmotic agents that were tested. In addition, actual osmotic distillation experiments were performed (using NaCl as the osmotic agent) at relatively high flows (50 L/h) in order to neglect thermal effects [26]. The osmotic distillation membrane used for testing was a capillary module supplied by Microdyn-Nadir GmbH^{TM} (LM2P06) [26]. The results from this portion of the study showed that $CaCl_2$ was the most effective; however, there are advantages to using glycerol and PG such as the lack of scaling and corrosion effects as well as comparable water flux rates. The driving force is restricted for NaCl because of its low solubility, although at low concentrations sodium chloride was determined to be equivalent to calcium chloride, shown in Figure 5 [26]. Additionally, increasing the driving force and flux resulted in significant concentration polarization; this effect of concentration polarization was shown to be relatively equal for the various extraction solutions that were tested [26].

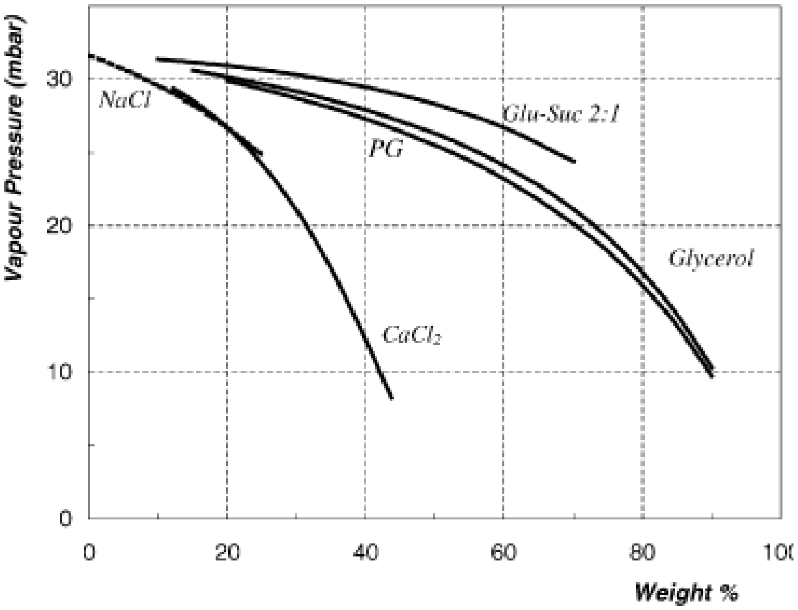

Figure 5. Vapor pressure versus concentration [26]. (Reprinted with permission from Elsevier.)

3.2.3 Concentration Polarization

Based on a literature survey by Gryta, 2005, concentration polarization is an important factor in osmotic distillation (especially on the osmotic agent side of the membrane) [6]. As the water flux increases, the impact of concentration polarization increases [6]. When concentration polarization occurs, or when boundary layers form along the surface of both sides of the membrane, the water activity, and flux can significantly decrease. The influence of concentration polarization is the reason that the module design is very important for obtaining optimal hydrodynamic conditions [6]. According to Gryta, 2005, some authors assume that applying a temperature gradient in osmotic distillation (similar to DCMD) reduces the solute concentration of the liquid along the membrane surface resulting in a high flux [6]. In this case, complete concentration polarization occurs, which means that the driving force is a temperature gradient rather than a vapor pressure gradient and almost pure water is on both surfaces of the membrane [6,12].

3.2.4 Temperature Polarization

Another important factor in osmotic distillation is temperature and temperature polarization. If the membrane does not have a high thermal conductivity, there will be a substantial difference in temperature between the feed and osmotic agent. In osmotic distillation systems, the boiling point of the feed solution increases as the feed becomes more concentrated. The temperature of the feed then decreases as latent heat is absorbed, and the temperature of the osmotic agent increases as the latent heat is released [5,6]. The difference in temperature between the two sides of the membrane can cause the system to stall if the membrane is not thin or conductive. When the system stalls, there is no longer mass transfer across the membrane. The driving force in osmotic distillation is the difference in vapor pressure between the two contacting liquids. This driving force changes when a temperature gradient occurs causing a significant reduction in water flux.

3.2.5 Temperature Gradient

Courel *et al.*, 2000, studied the influence of operating parameters on the water flux for treating sucrose solutions using osmotic distillation [7]. The flux rates studied ranged from 0.5 to 23 kg/m^2h, which were obtained by varying the concentration, flow rates, and fluid temperatures. The study was conducted by treating sucrose feed solutions with concentrations up to 65 w/w % and by using an OA concentration of 45.5 $CaCl_2$ w/w % [7]. The membrane used was a flat-sheet commercial microfiltration membrane supplied by Pall-Gelman (TF200), which was made with thin porous polytetrafluoroethylene [7]. The two liquid solutions circulated co-currently though the flat sheet membrane. The results showed that the addition of a temperature gradient caused a moderate increase in flux. The concentration of the solute in the feed and the OA was determined to have the largest impact on mass transfer. An increase in osmotic agent concentration resulted in an increase in water activity and flux, as shown in Figure 6. Furthermore, the results showed that as the sucrose concentration in the feed increases, the vapor flux decreases. This reduction in vapor flux was due to the increase in viscosity and the reduction in transport properties or osmotic potential of the solutions [7]. Courel *et al.*, 2000, recommends further research on improving the hydrodynamic conditions, which would assist in determining the benefits of using a combined concentration and temperature gradient in order to optimize performance [7].

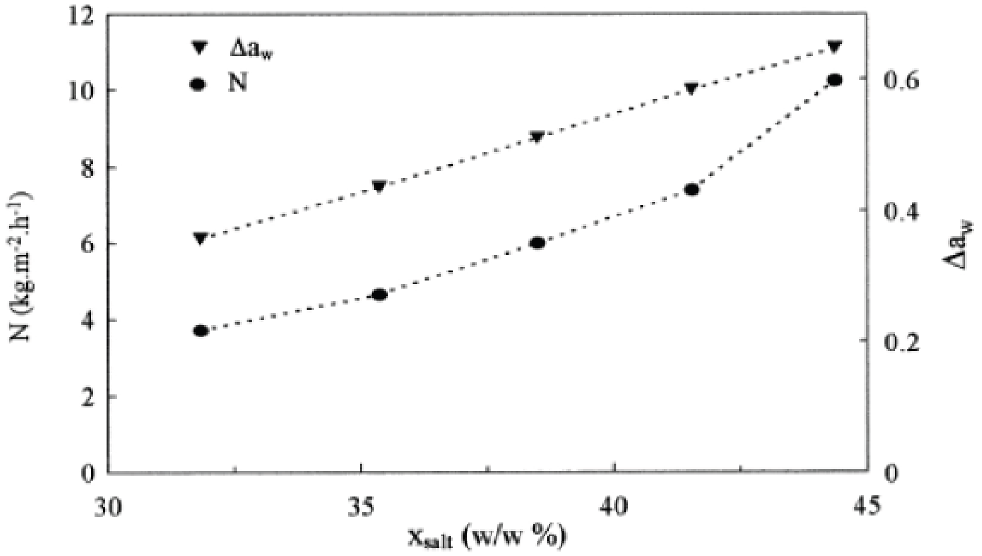

Figure 6. Vapor flux (N) and water activity versus composition [7]. (Reprinted with permission from Elsevier.)

3.2.6 OD Model Development

Romero *et al.*, 2003, developed a model for mass and heat transfer in osmotic distillation [8]. The model was developed based on four resistances in series, which takes into account the several boundary layers that form in OD. This model specifically predicted the flux rates based on temperature, concentration, and flow rates. To determine the accuracy of the model, the predicted values were compared to experimentally determined data provided by Courel, 1999 [8,35]. The results showed that an increase in the OA concentration and flow rate resulted in an increase in flux. Additionally, temperature was determined to be an important parameter, as when the temperature increased the water flow also increased. Based on simulations for spatially varying temperature and isothermal conditions, temperature polarization appeared to cause a 15–20% decrease in water flux due to a decrease in driving force [8]. The results also showed that the predicted water flux is always less than the experimental values across a range of vapor layer thicknesses or hydrophobic layers, as shown in Figure 7 [8]. Figure 7 shows the flow rate of the osmotic agent versus the water flux for the simulated and experimental data. The difference between the values predicted by the model and the actual experimental data may be due to membrane geometry and liquid penetration (i.e. some loss in hydrophobicity) [8].

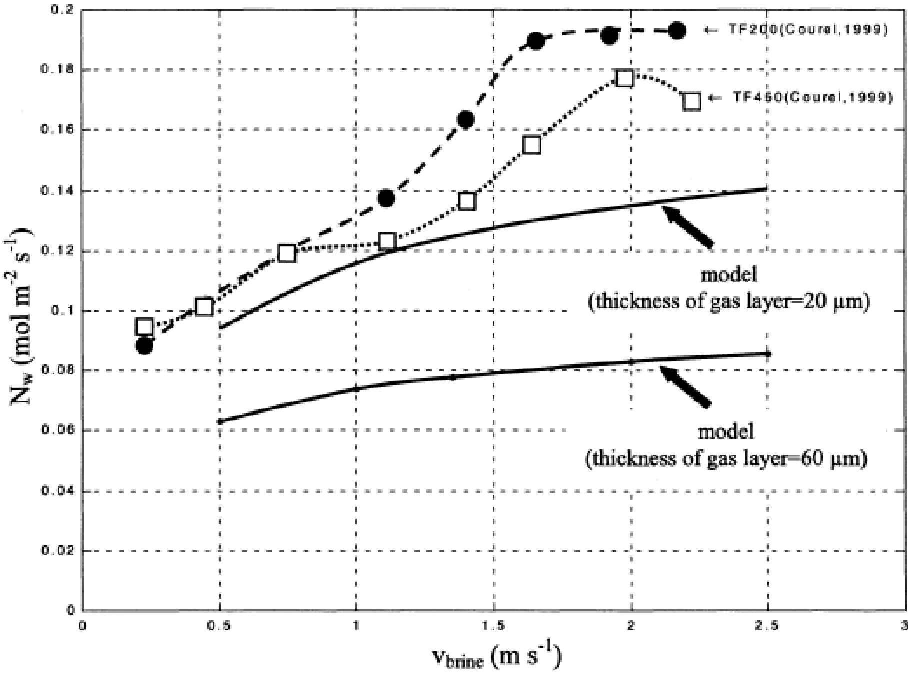

Figure 7. The water flux versus OA velocity at varying vapor layer thicknesses [8]. (Reprinted with permission from John Wiley and Sons.)

3.2.7 Membrane Geometry

The geometry of the membrane may affect the hydrodynamics, such as turbulent nature of the flow [8]. Flow rate or pressure of the liquids play an important role in liquid penetration in the membrane structure, which can significantly affect boundary layer thickness or mass-transfer resistance [8]. An increase in pressure affects the penetration depth as well as the thickness of the water vapor layer. The pore size, contact angle, and surface tension of the liquids influence how far the liquid streams are able to penetrate within a pore as well. As the concentration of the osmotic agent increases, the surface tension increases, the water activity decreases, and the osmotic pressure increases. Other factors that may influence membrane performance include membrane material, operating temperature and pressure, membrane surface charge, thermal conductivity, and contact time. The contact time is dependent upon membrane design or surface area. As the surface area of the membrane increases, the contact time increases, and the flux increases.

Troger *et al.*, 1998, studied the surface tension of the solid material used in microporous hydrophobic membranes by using wetting kinetics [9]. Materials with different porosities were investigated, which included polypropylene, polyethylene and polytetrafluoroethylene. A series of alkanes with varying surface tensions were used to test the membrane materials [9]. In the study, experimental data were analyzed by using a modified Washburn equation, as shown in Equation 8.

$$m^2(t) = (c\bar{r})A^2\epsilon^2\frac{\rho_L^2\gamma_L\cos\theta}{2\eta}t = K\frac{\rho_L^2}{2\eta}\gamma_L\cos\theta t \qquad \text{Equation 8}$$

By plotting normalized penetration rates versus liquid surface tension, the maximum of the curve (when the surface tensions of the solid and liquid are equal) determines the surface tension of the solid [9]. The results showed that the modified equation provides relevant estimations of surface tension values for various membrane materials. The study also showed that pore geometry does not have a significant impact in the location where the maximum occurs. Based on the research conducted by Troger *et al.*, 1998, interactions between liquids and solid materials are an important factor in membrane design; surface tension values for different materials vary and affect liquid penetration.

3.2.8 Pore Size

Babu *et al.*, 2006, studied mass transfer in osmotic distillation by using sweet-lime juice and phycocyanin colorant [10]. The research focused on the effect of concentration, flow rates of the two liquids, and pore size of the membrane on flux. A flat-plate polypropylene membrane was used with different pore sizes (0.2 µm and 0.05 µm). The study showed that the diffusion regime was between molecular diffusion, where molecule-molecule collisions dominate, and Knudson mechanism (molecule-wall collisions dominate) [10]. Molecular diffusion played a greater role with a membrane pore size of 0.2 µm (59%), whereas, when the pore size was 0.05 µm Knudson diffusion had a higher contribution (74%) [10]. Although the mass transfer mechanism did not show a large dependence on pore sizes between 0.05 µm and 0.2 µm; for a larger pore size of 1.0 µm the water flux increased significantly. This increase in water flux was most likely due to molecular diffusion [10]. Additionally, the results showed that at low feed concentrations, the flow rate did not have a significant impact on flux for both feed solutions.

3.3 Summary

The mechanisms that affect osmotic membrane distillation are very complex; heat and mass transfer phenomena occur simultaneously, which make it difficult to determine specific parametric influences. In order to optimize the performance of OD membranes, it is imperative that one also fully understands the mechanisms that take place. Models have been developed to predict the effects of parameters; however, hydrodynamics, membrane geometry, and liquid penetration are all potential factors that make it difficult to develop accurate models. Experimental results based on a number of studies covered here have shown that temperature, concentration, polarization phenomena, and flow rates all have an impact on vapor flux. Previous research has also shown the importance of membrane material, surface tension (both solid and liquid), liquid penetration depth, pore size, and extraction solution composition. In general, these studies (experimental and simulated) were focused on flux and achieving high quality concentrate or feed. This study however was based on the quality of the extracted water or TOC rejection. The results from this research contribute to further understanding osmotic distillation by demonstrating the effect the osmotic agent and pH of the feed on total organic carbon rejection.

CHAPTER FOUR
HYPOTHESIS/OBJECTIVES

The mechanisms that affect osmotic membrane distillation performance are complex. Specific parametric influences are difficult to determine due to simultaneous heat and mass transfer phenomena. Previous research has shown that membrane material, surface tension (both solid and liquid), and pore size have an effect on liquid penetration depth and performance [8–10]. Studies have also shown that water flux is influenced by flow rate, temperature, concentration, and polarization phenomena [6–8,10–17,29]. Studies have not been conducted on the effect of osmotic agent concentration and pH of the feed solution on TOC rejection.

4.1 Research Hypothesis

In previous testing, the osmotic distillation system used in this study appeared to achieve an increase in TOC rejection as the concentration of the osmotic agent increased [2]. This relationship was thought to be due to the solubility of semi-volatiles and water activity, which may be influenced by the OA concentration. The hypothesis studied in this thesis was that osmotic agent concentration and pH of the feed influence TOC rejection in osmotic distillation. One particularly important parameter was pH because NASA is considering changing the standard feed pretreatment approach and proposing changing the feed pH. The results from this study were used to test this hypothesis.

4.2 Research Objectives

The objective of this study was to determine the effect of the ionic strength of the osmotic agent and pH of the feed solution on TOC rejection. This was important for evaluating NASA's standard feed treatment approach as well as determining the optimal operating conditions of the OD system. In order to optimize the performance of the OD system, it is important to distinguish significant parameters and to understand the mechanisms that occur in osmotic membrane distillation. This study contributes towards the development of an optimal design and further understanding of osmotic distillation technology.

CHAPTER FIVE
MATERIALS AND METHODS

5.1 Test Apparatus

One of the primary tasks that needed to be completed before conducting experiments was to build an OD prototype. This required redesigning an existing OD system and building the system. Development of the OD system is a NASA-funded project to evaluate the technology for future space flight applications. Before tests could be initiated, it was necessary to complete all electrical, process control, plumbing, and fabrication. Figures 8 and 9 show the OD system that was used for testing from 2007 to 2009 [2,3]. The new OD prototype is shown in Figure 10. Several important editions to the new OD system were added specifically to address issues that occurred with the previous system. The specifications for the main components of the OD system are shown in Table 1.

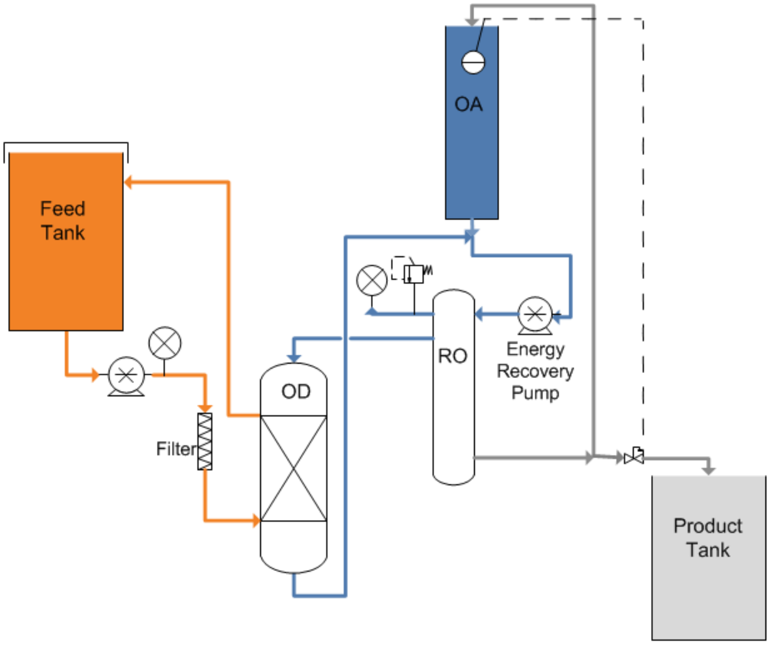

Figure 8. Osmotic distillation process flow diagram used for 2007–2009 testing [2,3].

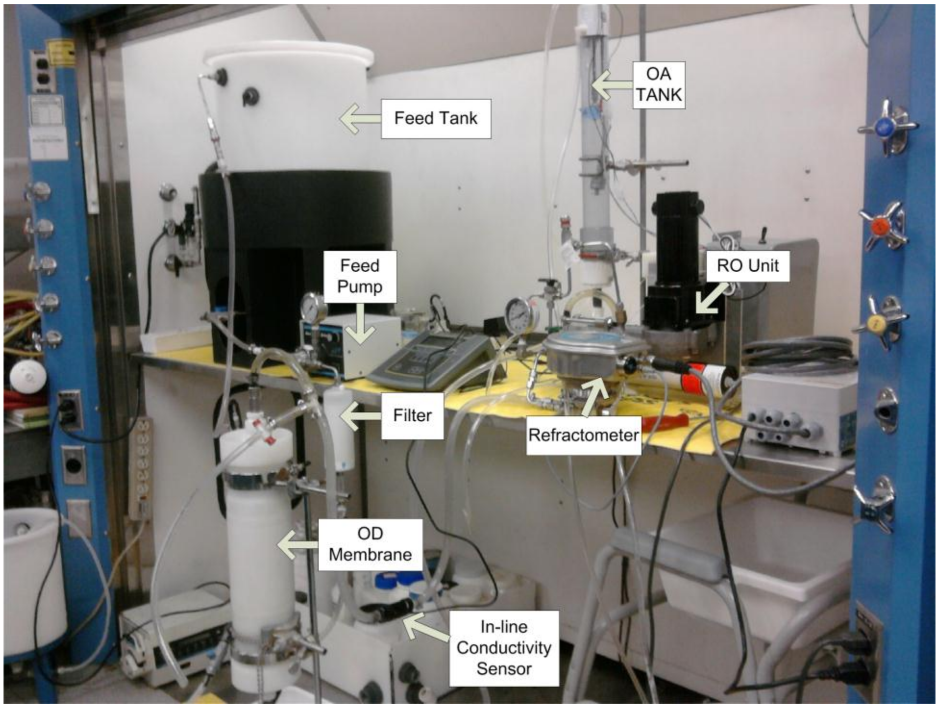

Figure 9. OD system used for 2007–2009 testing [2,3].

Front

Back

Figure 10. New OD prototype.

Table 1. Equipment specifications.

Component		
RO Desalinator		
Model	Katadyn Powersurvivor 40E	
Membrane*:	(Dow) Filmtec SW30HR-1713, GMID 80753	
Membrane Type	Polyamide Thin-Film Composite	
Flow Limits	58.5 ± 15	GPD
Minimum % Rejection	97	%
Recovery	2.5	%
Maximum Operating Pressure	1000	psi
Maximum Operating Temperature	45	°C
Maximum Pressure Drop	15	psig
OD Membrane		
Model	Liqui-Cel X50 (4 x 13 Extra Flow)	
Flow	0.7 – 3.4	m^3/hr
Pore Size	0.04	µm
Nominal Wall Thickness	40	µm
Porosity	40	%
Material	Polypropylene	
Filter	Whatman Polycap HD model 2814T	
Total System Performance		
Power	100 to 350 W-hr/L	
Mass	25 kg/ 1st person + 2.6 kg/additional person	
Volume	0.27 m^3/ 1st person	
TOC rejection	99%	
Recovery	55 – 80% (potentially up to 93%)	
Flow	0.06 – .15 kg/hr	

* For test conditions 32,000 ppm NaCl at 25 °C and 800 PSI

Figure 11 shows the process flow diagram for the new OD prototype. The two important new features of this system include the brine resupply tank and the electronic proportioning valve. The brine resupply tank contained a concentrated salt solution (27 g NaCl/100 mL DI water). The concentrated brine was pumped into the OA stream in order to maintain a specific concentration value or set-point. An inline conductivity sensor was used to measure the concentration of the osmotic agent. Based on this value, the concentrated brine was pumped into the OA stream until the set-point is reached. A solenoid pump was used to pump 20 µL per pulse of the concentrated brine as shown in Figure 12. The purpose of the brine resupply tank was to maintain the concentration of the osmotic agent at a set-point. This system is required because the RO membrane continuously loses salt to the product and the rate of salt lost increases as the RO membrane ages.

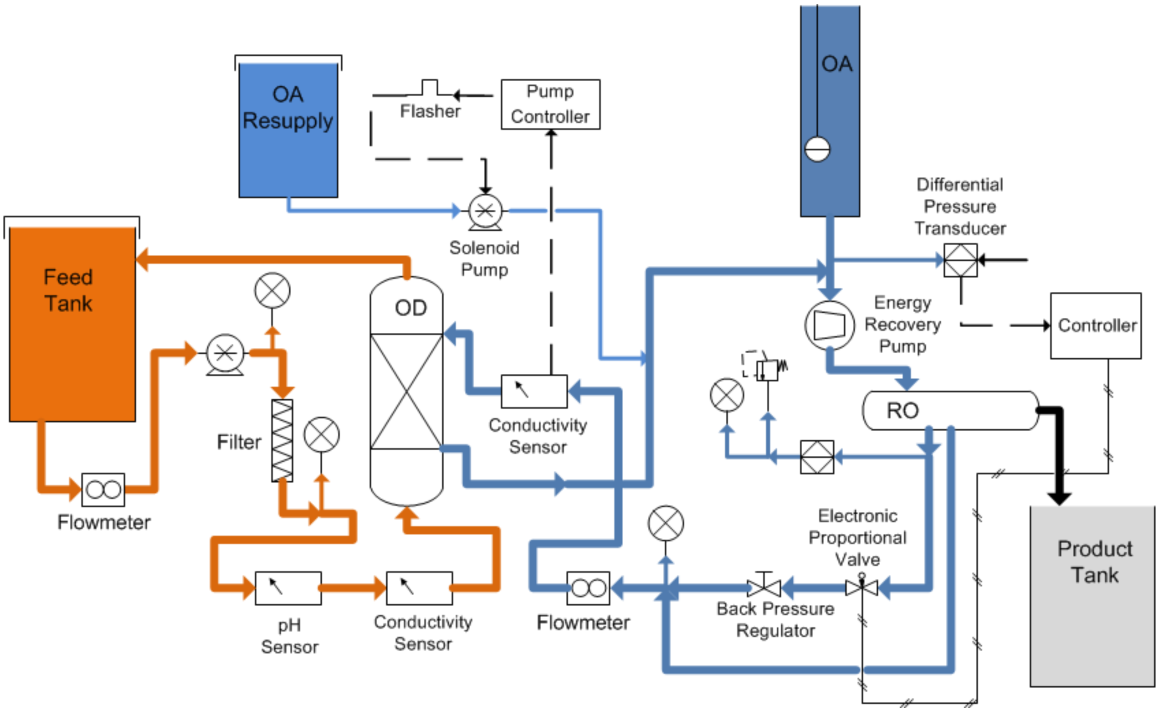

Figure 11. Process flow diagram for OD prototype.


Figure 12. Flasher and micro-pump.

The second important new feature of the OD system was the electronic proportioning valve. A differential pressure transducer (shown in Figure 13) sends a signal to a controller by measuring the hydrostatic pressure of the osmotic agent (or essentially the liquid level of the OA in the osmotic agent tank). Depending on the liquid level set-point, the controller sends a signal to the automatic valve, which controls the pressure within the RO unit, as shown in Figure 14. By controlling the RO pressure or the flow through the RO membrane, the production rate of the RO unit was controlled. The reason that the electronic proportioning valve was important was because the production rate of the OD membrane does not equal the production rate of the RO unit; the RO unit produces 5.6 liters/hour. Therefore, without the electronic proportioning valve the system could not be controlled. The level in the OA tank would significantly drop as the run progressed until the tank was completely empty.

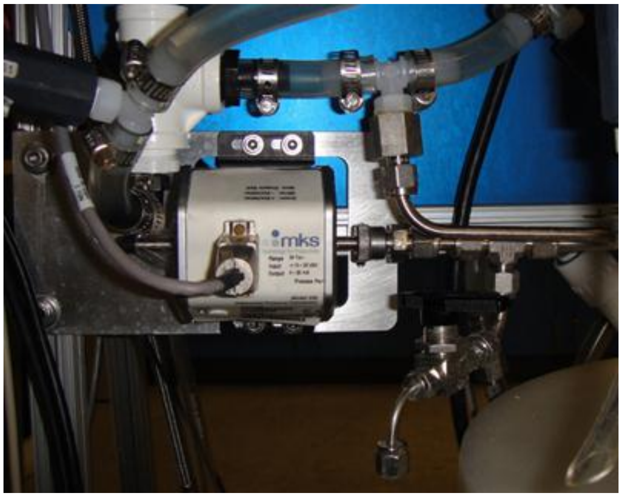

Figure 13. Differential pressure transducer.

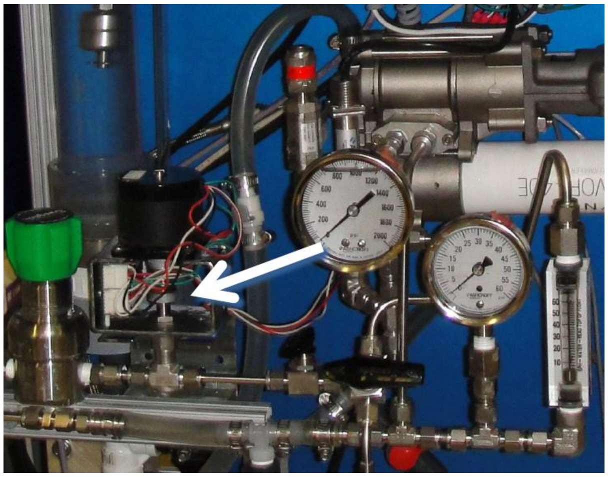

Figure 14. Electronic proportional valve.

5.2 Protocol for Testing

The experiments and sample analysis were conducted at NASA Ames Research Center. The feed composition was based upon the transit mission wastewater ersatz standard formulation determined for testing wastewater treatment systems intended for human space flight [1]. Transit mission wastewater roughly consists of 33.4% w/w human urine, 46.3% w/w humidity condensate, and 9.1% w/w urine flush water, as shown in Table 2 [1]. The feed used for testing consisted of simulated urine, humidity condensate, and urine flush water. The feed volume used for each test was 8.0 L.

The simulated urine organics (concentrate 1), urine inorganics (concentrate 2), and humidity condensate (concentrate 3) solutions were prepared using the components and concentrations shown in Tables 3, 4 and 5 respectively [1]. According to Verostko *et al.*, 2004, the substances in the humidity condensate (Table 5) were based upon the analysis of Space Station humidity condensate, which was conducted by Marshall Flight Space Center (MFSC) [1]. Only 49% TOC was accounted for in the analyses and due to this discrepancy, Verostko *et al.* increased or adjusted the known organic substance concentrations to account for the undetected TOC [1].

Table 2. Transit mission wastewater composition.

	kg/person-day	Dilution Factor
Urine	1.18	2.99
Urine Flush (DI water)	0.32	11.03
Humidity Condensate	1.61	2.19

* Dilution Factor (mission total volume/waste stream component volume)

Tab1e 3. Composition of urine organics.

Name	Formula	MW	Concentrate (g)
Urea	NH_2CONH_2	60.06	52.021
Creatinine (98%)	$C_4H_7N_30$	113.1	5.221
Histidine, soluble (98%)	C_6H_9N3O2	155.2	0.958
Taurine	$C_2H_5NSO_3$	125.1	0.556
Glutamic acid	$C_5H_9NO_4$	147.1	1.66
Glucose (96%)	$C_6H_{12}0_6$	390.4	2.636
Ammonium citrate (99%)	$(NH_4)2C_6H_50_7$	226.2	12.34
Ammonium formate	NH_4HC0_2	63.1	1.466
Ammonium oxalate monohydrate	$(NH_4)_2C_20_4$	142.1	0.665

Tab1e 4. Composition of urine inorganics.

Name	Formula	MW	Concentrate (g)
Sodium chloride	NaCl	58.4	23.126
Magnesium chloride hexahydrate	MgCl26 · H2O	203.31	5.483
Potassium bicarbonate	KHCO3	100.1	2.197
Potassium carbonate	K2CO3	138.21	0.474
Potassium monobasic phosphate	KH2PO4	136.09	1.069
Potassium chloride	KCl	74.6	5.436
Potassium sulfate	K2S04	174.29	7.424
Calcium chloride	CaCl2	110.99	0.221
Sodium sulfate	Na2SO4	142	4.144

Tab1e 5. Composition of humidity condensate.

Name	Formula	MW	Concentrate (g)	Concentrate (mL)
Acetic acid	CH_3CO_2H	60.05	-	0.441
Benzoic acid	$C_6H_5CO_2H$	122.2	0.046	-
Benzyl alcohol	$C_6H_5CH_2OH$	108.14	-	0.259
Ethanol	C_2H_6O	46.07	-	1.506
Acetone	CH_3COCH_3	58.08	-	0.030
Caprolactam	$C_6H_{11}NO$	113.16	0.191	-
Phenol	C_6H_5OH	94.11	0.027	-
N,N-Dimethylformamide	$HCON(CH_3)_2$	73.1	-	0.035
Ethylene glycol	$HOCH_2CH_2OH$	62.07	-	0.157
4-Ethyl morpholine	$C_6H_{13}NO$	115.18	-	0.072
Formaldehyde (37%)	$HCHO$	30.03	-	0.461
Formic acid (96%)	HCO_2H	46.03	-	0.208
Lactic acid	$CH_3CH(OH)CO_2H$	90.08	-	0.187
Methanol	CH_3OH	32.04	-	0.218
1,2-Propanediol	$C_3H_8O_2$	76.09	-	0.013
2-Propanol	$(CH_3)_2CHOH$	60.1	-	0.042
Propionic acid	$CH_3CH_2CO_2H$	74.08	-	0.042
Urea	NH_2CONH_2	60.06	0.101	-

5.2.1 Preparation

Simulated urine and humidity condensate were prepared based on the transit mission wastewater ersatz formulation and preparation procedure determined by Verostko *et al.* [1]. The preparation procedure provided by Verostko *et al.* was followed rather than using Table 2, which shows the mission waste stream make-up values. The actual volume for each component to make up an 8.0 L solution is shown in Table 6. Sabatier and urine pretreatment concentrates were not included in the feed mixture for this study. The urine (organics and inorganics) and humidity condensate concentrates were prepared prior to testing and stored under ambient conditions. The osmotic agent solution consisted of NaCl in deionized water. The pH of the feed was adjusted to the desired pH by adding phosphoric acid or potassium hydroxide. Flocon 260™, an antiscalant/antifoulant, was also added to the feed. Once the feed was prepared, a 25 mL sample was analyzed for ions, TOC concentration, and pH. These values were compared to the transit wastewater ersatz water quality targets shown in Tables 7 and 8 to indicate whether the solution was made correctly.

Table 6. Component volume for 8.0 L feed solution.

Component	Volume (mL)
Concentrate 1 (10X) Urine Organics	800
Concentrate 2 (10X) Urine Inorganics	800
Concentrate 3 (10X) Humidity Condensate	800
DI Water	5600

Table 7. Transit wastewater ersatz water quality targets.

pH	Conductivity µS	TOC mg/L	TIC mg/L
2.6 ± 0.2	12352 ± 1853	2209 ± 221	0 ± 0

Table 8. Transit mission ersatz water ion targets.

Ion	mg/L
Cl	1870 ± 281
NO_2^- N	-
NO_3^- N	-
PO_4	75 ± 11
SO_4	2864 ± 430
Na	1045 ± 157
NH_4^- N	221 ± 33
K	1387 ± 208
Ca	7.95 ± 1.2
Mg	64.0 ± 10

5.2.2 Experimental Design

A 3x3 matrix was used for the basis of the experimental testing. Nine experiments were completed. Additional experiments or repeated runs were conducted based upon the trends and results from the nine experiments. The duration of each test was approximately 45 hours to ensure that the system reached steady state and to collect a sufficient number of feed, OA, and product samples. The pH values studied include 3, 7, and 10, and the osmotic agent concentrations were 20, 30, and 40 g/L.

The order that experiments were completed is shown in Table 9. In order to prevent biased results the order that the experiments were conducted was determined randomly. The pH range chosen for testing was based on the manufacturer's specifications of the osmotic distillation membrane. The Liqui-Cel™ OD membrane tolerates liquids at a pH of 2.5–10 and the RO membrane pH tolerance range for continuous operation was 2–11. The OA salt concentration was determined by osmotic pressure limitations for the reverse osmosis membrane unit; the maximum membrane pressure is 1000 psi and 45 g/L would exceed this pressure limit.

Table 9. Experimental design.

	Design Variables				Response Variable
Run	Feed pH	OA [NaCl] g/L	Feed Volume mL	Feed Flowrate gpm	TOC ppm
1	3	20	8000	0.9	
2	7	30	8000	0.9	
3	10	30	8000	0.9	
4	10	40	8000	0.9	
5	7	40	8000	0.9	
6	10	20	8000	0.9	
7	7	20	8000	0.9	
8	3	30	8000	0.9	
9	3	40	8000	0.9	

The fixed parameters for an individual run include the feed flowrate, pH, OA concentration, and initial feed volume. During each test, the feed pH and the osmotic agent salt concentration were controlled. A controller and a solenoid pump were used to pump a concentrated solution of sodium chloride (27 g/ 100 mL) into the OA stream in order to control the OA concentration. Phosphoric acid or potassium hydroxide was added (manually) to the feed tank to control the pH when the value was greater than or less than 0.20 pH units of the set-point. After the acid or base was added to the feed, the tank was mixed to prevent fluctuations in pH readings. Product, OA, and feed samples (25 mL) were taken at the beginning and end of the normal working hours of a test. The system operated continuously including overnight during which time samples were not collected. When an OA sample was taken, an equal amount of product was added to the

OA tank to maintain the liquid level and normal operation of the system. The 10-25 µm pre-filter for the feed was replaced after every two runs.

Several operating conditions were documented for each test including the OA chloride concentration, OA conductivity, product volume, and pressure (feed and OA) as shown in Table 10. After the completion of a test, the OD system was rinsed in deionized water (minimally four times) and then stored in a solution composed of 1000 ppm sodium metabisulfite (0.1% w/v sodium metabisulfite and 99.9% DI water) over the weekend. Before the start of each new test, the system was rinsed two times (minimally) with deionized water in order to flush out the sodium metabisulfite.

Table 10. List of measured and recorded variables.

Variable	Symbol	Units
Time	t	hr:min
RO/OA Pressure	P_{OA}	psi
OA Conductivity	EC_{OA}	mS/cm
OA Resupply Volume	OA_{RS}	mL
Product Volume	$V_{product}$	mL
pH of the Feed	pH_{feed}	pH
pH of the OA	pH_{OA}	pH
pH of the Product	$pH_{product}$	pH
Product Conductivity	$EC_{product}$	mS/cm
Feed' Conductivity	EC_{feed}	mS/cm

5.3 Analytical Instruments and Sample Analysis

The NASA Ames Central Analytical Chemistry Laboratory conducted the sample analysis in compliance with standard detection limits and analysis procedures based on the Standard Method for Examination of Water and Wastewater, as shown in Table 11

[36]. Each sample was analyzed for TOC concentration, pH, and ions. Specific ion concentrations were determined by following Standard Method 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity) [36]. The analytical instruments for the sample analysis are shown in Table 12. Torrent Laboratory, Inc. conducted sample analysis using Method E415.1 (Total Organic Carbon Combustion or Oxidation) for samples with high a high chloride concentration such as the OA.

Table 11. Standard methods and limits.

Instrument		Standard Method	Limits
pH Detector	4500H$^+$ B	Electrometric Method	
TOC Analyzer (TOC-VWS/P)	5310C	Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method	Interference if above 0.05% of Cl^-
TOC Analyzer (TOC-V CSH)	5310B	Total Organic Carbon (Combustion or Oxidation) Method	Precision: 10–15 %
Ion Chromatograph for Cations	4110 B	Ion Chromatography with Chemical Suppression of Eluent Conductivity	
Ion Chromatograph for Anions	4110 B	Ion Chromatography with Chemical Suppression of Eluent Conductivity	

Table 12. Analytical instruments.

Instrument / Hardware	Manufacturer	Model
pH Detector		
pH Pump Control System	Etatron	DLX pH/M (I/h bar: 8-10)
Double Junction pH Electrode	Cole-Parmer	Part No. 27301-20
TOC analyzer	Shimadzu	TOC-VWS/P
TOC analyzer	Shimadzu	TOC-V CSH
Ion Chromatograph for Cations	Dionex	ICS-1500
Ion Chromatograph for Anions	Dionex	DX-500

5.4 Data Analysis

Graphical analysis was used to determine the relationships, trends, and interactions between the sets of data. The TOC concentration was plotted versus time based on pH values and OA salt concentrations. The water recovery ratios and water production rates were also determined. The water recovery ratios were calculated by dividing the volume of product by the volume of feed. The data were analyzed by determining the standard deviation, as shown in Equation 9 and 10 respectively. The standard error shown in Equation 11 was also calculated based on 95% confidence limits. Error bars were plotted with the data.

$$s^2 = \sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1} \qquad \text{Equation 9}$$

$$s = \sqrt{s^2} \qquad \text{Equation 10}$$

$$SE = \frac{s}{\sqrt{n}} \times 1.96 \qquad \text{Equation 11}$$

CHAPTER SIX
RESULTS

The hypothesis was that osmotic agent concentration and pH of the feed influence TOC rejection in osmotic distillation. The effect of the ionic strength of the osmotic agent and the pH of the feed solution on TOC rejection was determined. Tests were conducted at selected OA concentrations (NaCl in DI water) and pH values of the feed using phosphoric acid and potassium hydroxide. The pH values studied included 3, 7, and 10, and the osmotic agent concentrations studied were 20, 30, and 40 g/L. A 3x3 matrix was used for the basis of the experimental testing; therefore, nine experiments were completed along with four repeated runs to provide statistically valid data sets. The duration of each test was approximately 45 hours.

6.1 Experimental Results

Figure 15 shows the TOC concentration of the osmotic agent over time for all runs. Although there is scatter in the data, the pH 3 feed experiments clearly resulted in significantly higher TOC concentrations in the osmotic agent when compared to the feed pH values of 7 and 10. The pH 3 experiments resulted in the highest TOC concentrations in the osmotic agent, which ranged from approximately 70 to 130 ppm. There was little or no difference in the TOC rejection values between the experiments with a feed pH of 7 and a feed pH of 10.

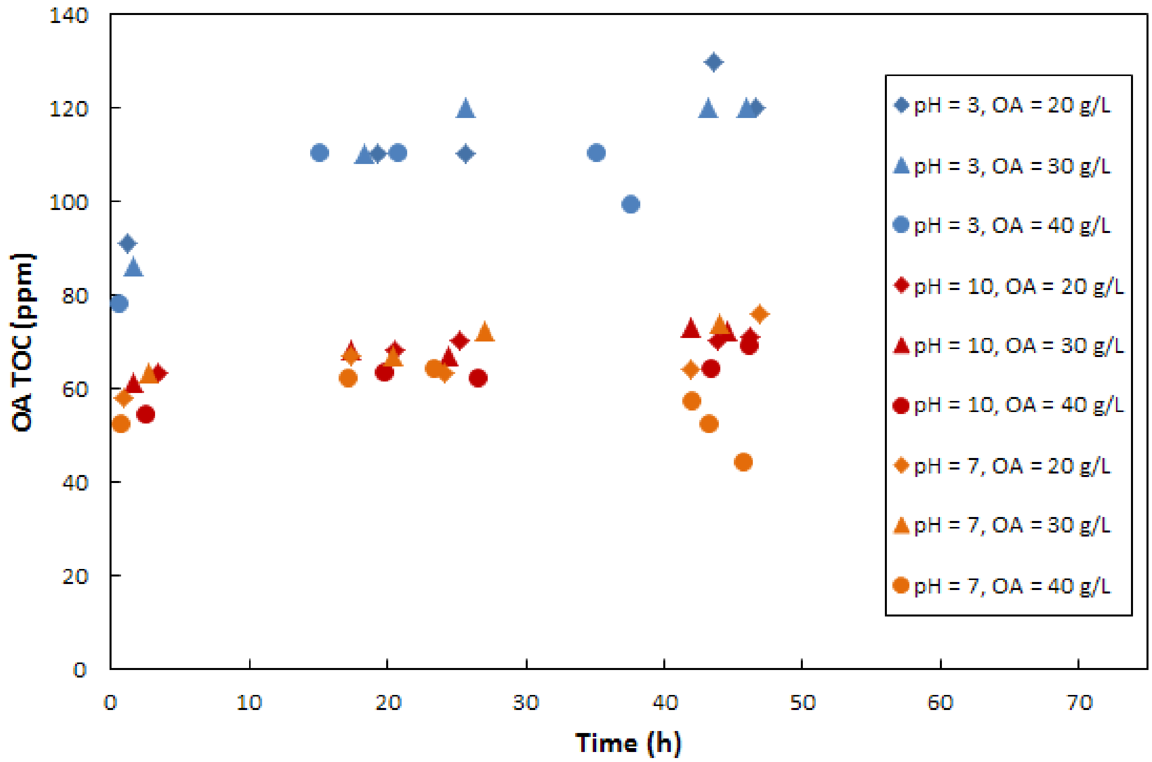

Figure 15. TOC of the osmotic agent versus time for pH 3, 7, and 10 with OA concentrations of 20, 30, and 40 g/L NaCl.

Figure 16 shows the TOC concentration of the osmotic agent for the feed pH values of 3, 7, and 10 and an osmotic agent concentration of 20 g/L. This figure shows that the experiments with a feed pH of 3 resulted in significantly higher TOC concentrations in the osmotic agent than the experiments with a feed pH of 7 and 10. However, the experiments with feed pH values of 7 and 10 showed similar TOC concentrations throughout the entire duration of the experiment.

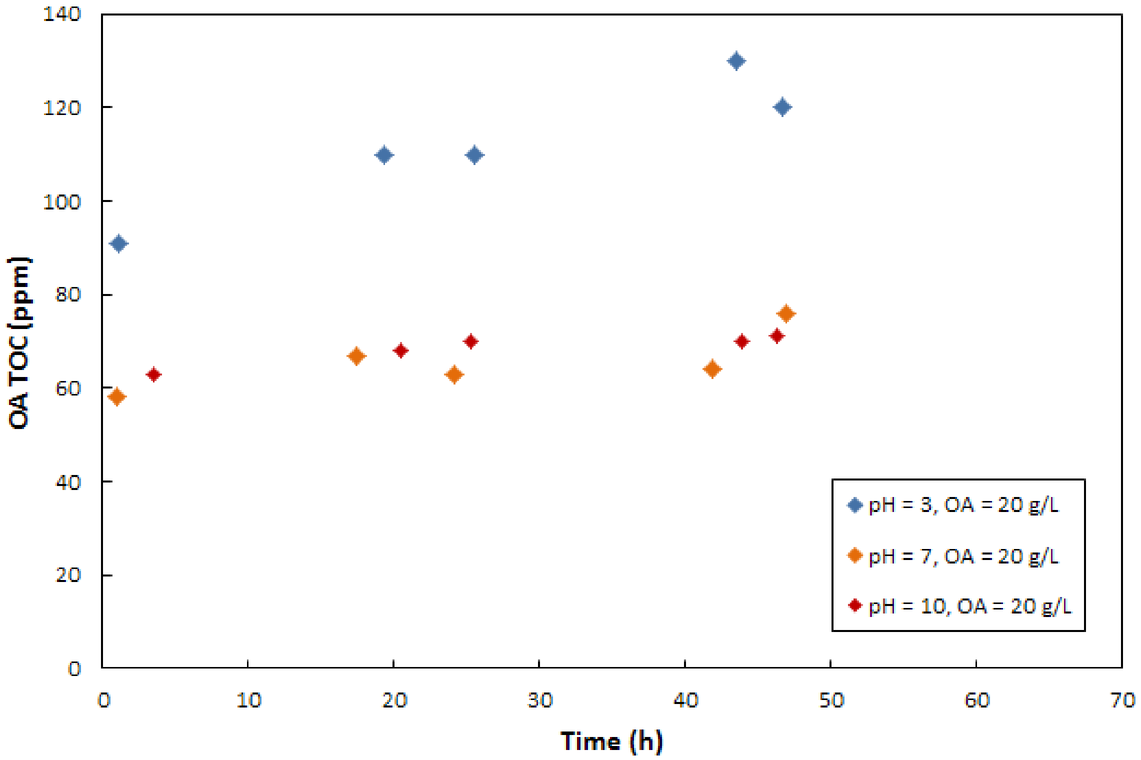

Figure 16. TOC of the osmotic agent versus time for pH 3, 7, and 10 with OA concentrations of 20 g/L NaCl.

Figure 17 shows the TOC concentration of the osmotic agent versus the water recovery ratio for the experiments with feed pH values of 3, 7, and 10 as well as an osmotic agent concentration of 40 g/L. The maximum osmotic agent concentration studied was 40 g/L. The experiments with OA concentrations of 40 g/L resulted in the highest water production rates when compared to the experiments with osmotic agent concentrations of 20 and 30 g/L. These experiments also had the highest water recovery ratios because of the high water production rates. The experiment with a feed pH of 3 and an osmotic agent concentration of 40 g/L resulted in the highest production rates and recovery ratios with respect to all other experiments that were conducted. Additionally, due to the high water recovery ratios, this experiment ended prematurely when compared to experiments with a feed pH of 3 and an osmotic agent concentration of 20 and 30 g/L.

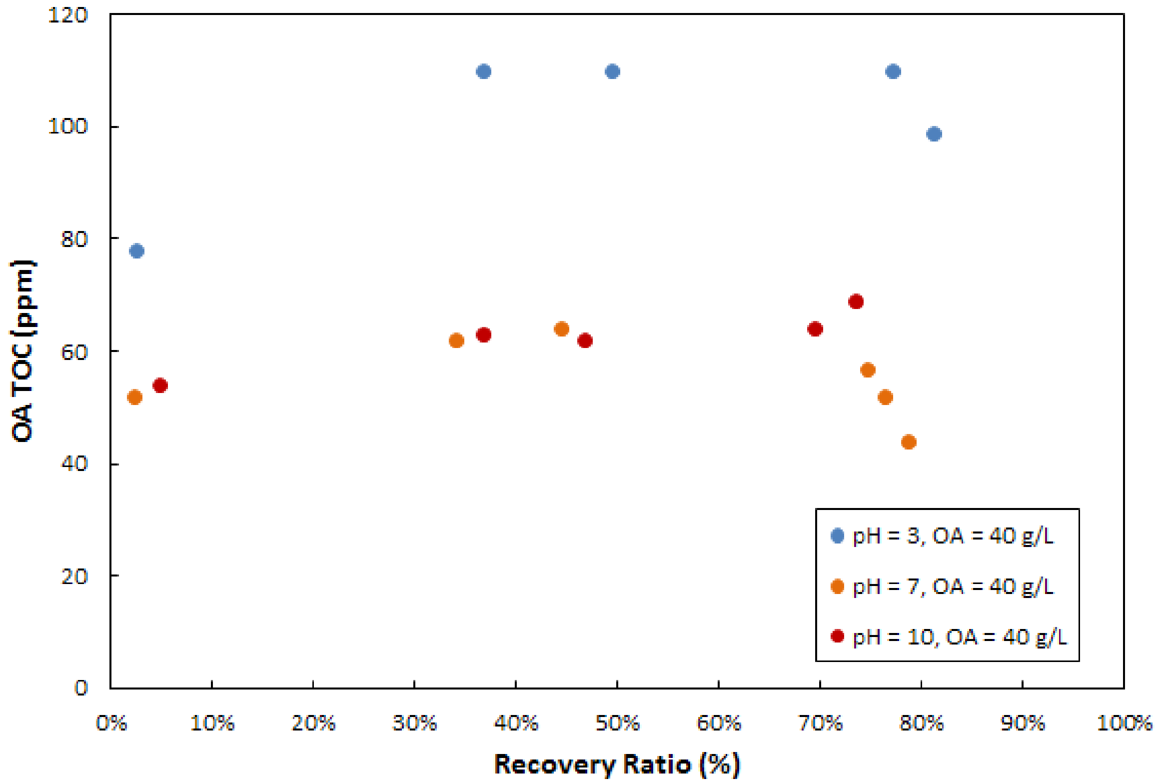

Figure 17. TOC of the osmotic agent versus recovery ratio for pH 3, 7, and 10 with OA concentrations of 40 g/L NaCl.

6.2 Statistical Analysis Results

Figure 18 shows the average TOC concentration of the osmotic agent versus time for the feed pH values of 3, 7, 10 and osmotic agent concentrations of 20, 30, and 40 g/L. Error bars were determined based on the standard deviation and standard error (with 95% confidence) for each set of pH data. The error represents the scatter in the complete set of data as a function of time. This figure verifies the conclusion that feed pH 3 data is statistically different from both pH 7 and pH 10 data.

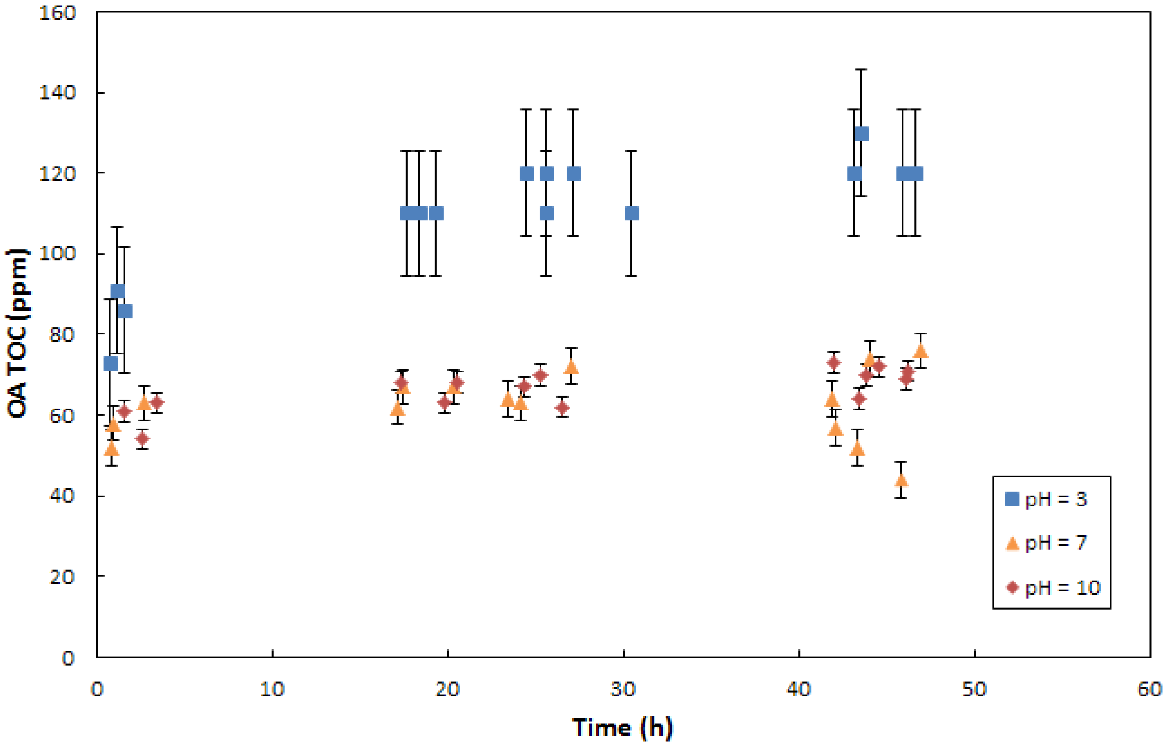

Figure 18. TOC of the osmotic agent versus time for pH 3, 7, and 10.

Figure 19 shows the average of three data sets from the repeated experiments with a feed pH of 3 and an osmotic agent concentration of 20 g/L and 40 g/L. Error bars were determined for each data point by calculating the standard deviation, and the standard error with a 95% confidence interval. Figure 19 shows that statistically there is no measurable difference in TOC rejection when comparing the osmotic agent concentrations of 20 g/L and 40 g/L. The results show that statistically the osmotic agent concentration does not have an effect on TOC rejection.

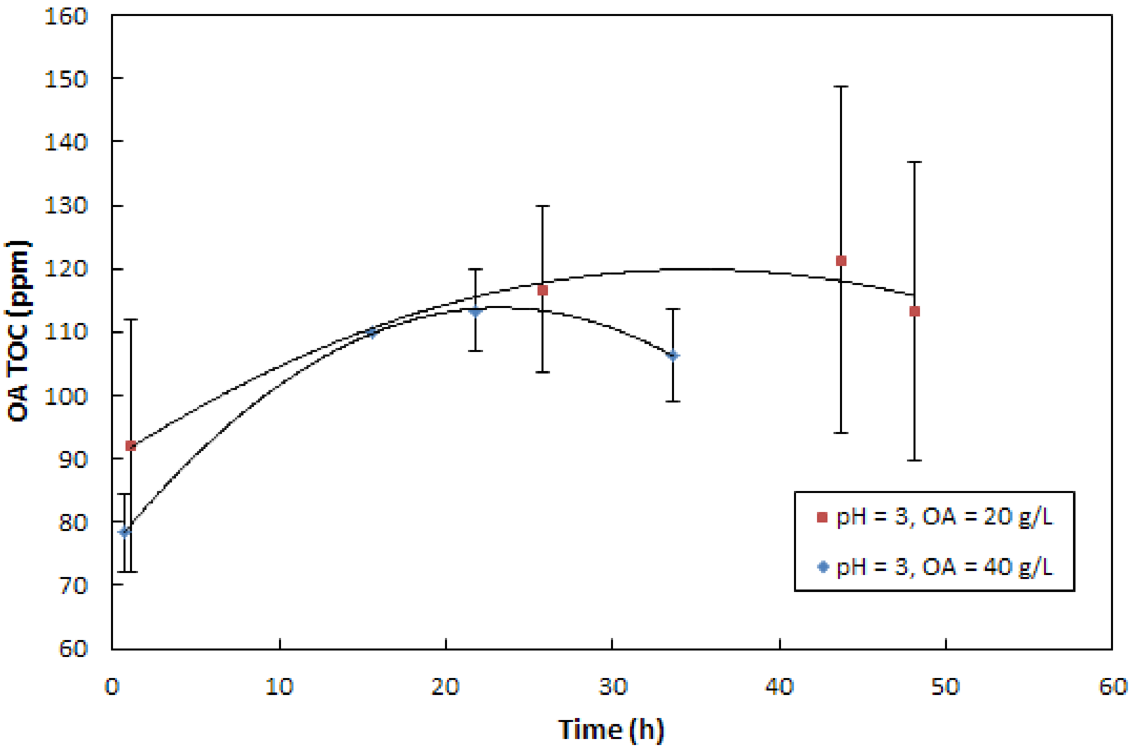

Figure 19. TOC of the osmotic agent versus time for pH 3 at 20 and 40 g/L.

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CHAPTER SEVEN
DISCUSSION

The hypothesis was that osmotic agent concentration and pH influence TOC rejection in osmotic distillation. The objective of this study was to determine the effect of the ionic strength of the osmotic agent and pH of the feed solution on total organic carbon (TOC) rejection in osmotic distillation. The results indicated that pH had an effect on TOC rejection in osmotic distillation. The experiments with a feed pH of 3 resulted in significantly higher TOC concentrations in the osmotic agent when compared to pH 7 and pH 10 experiments. The pH 7 and 10 feed experiments did not demonstrate a statistical difference in the effect of pH on TOC rejection. The results also indicated that at a feed pH value of 3, the osmotic agent concentration had no effect on TOC rejection.

Based on the literature review, this study is unique and cannot be directly compared to previous studies. Literature was not found on the relationship between the feed pH and TOC rejection. Literature was also not found on the relationship between osmotic agent concentration and TOC rejection. Of the few articles found, one [22] indicated a relationship between pH and the dissociation of compound classes in water.

Based on Tromans' research, as the inorganic solute concentration was increased, the solubility of oxygen in the liquid decreased [4]. The differences between Tromans' work and the research conducted in this study are the use of a semi-permeable membrane as well as heterogeneous volatile and semi-volatile components. A relationship was thought to exist between Tromans' study and the solubility of organic semi-volatiles and volatiles in the osmotic agent. However, the effect of ionic strength of the osmotic agent solution on the solubility of semi-volatile and volatile organics in the OA (or TOC rejection) remains unverified but is certainly very small if it exists at all.

7.2 Significance

In general, the results of this research are the foundation for future work that will be conducted for NASA. Determining the optimum operating conditions of the osmotic distillation system is necessary for future design considerations. This research contributes to a better understanding of osmotic distillation technology. Furthermore, this research shows that the pretreatment approach that NASA currently follows may be ill-advised.

Based on this study, pH has an important role in the performance of the OD system with respect to TOC rejection. NASA's pretreatment protocol requires a low pH of approximately 2, which was determined to prevent ammonia production, bacteria growth, calcium scale, and precipitation.

7.2.1 Ammonia and Bacteria

Over time, the urea in urine decomposes, which causes the feed solution to become alkaline and allows for microbial growth and solids to precipitate out of solution. Urease is an enzyme that catalyses the hydrolysis of urea into ammonia and carbon dioxide or ammonium carbonate, as shown in Equation 12 [37]. As the urea in the urine mixture decomposes, the pH of the feed solution increases, and the hydrogen ion concentration decreases. As a result, at an elevated pH ammonia is primarily produced rather than ammonium, as shown in Equation 13 [37]. At pH values below 6, ammonium is predominately produced rather than ammonia.

$$(NH_2)_2CO + H_2O \rightarrow CO_2 + 2NH_3 \qquad \text{Equation 12}$$

$$(NH_2)_2CO + 2H_2O + H^+ \rightarrow 2{NH_4}^+ + {HCO_2}^- \qquad \text{Equation 13}$$

7.2.2 Formation of Solids

Accumulation of calcium scale solids is another important issue due to the astronauts losing calcium in space through their urine. This loss in calcium results in the formation of calcium carbonate and calcium sulfate, which over time build up in the pipes connected to the toilet on the International Space Station (ISS). To address this issue, sulfuric acid is added to the urine, which was expected to prevent any scale from forming. However, sulfuric acid has resulted in the formation of calcium sulfate or solids in the ISS urine processor assembly (UPA). The UPA is a wastewater treatment process used for treating wastewater on ISS. This system has failed over time due to the formation of solids, which requires the system to be returned to earth for necessary repairs. By changing the pretreatment approach or the pH of the spacecraft wastewater, this issue of the formation of solids may be reduced. Additionally, this may also reduce the TOC concentration in the product water. This work has shown that replacing the sulfuric acid pretreatment with a less strong organic acid that does not produce sulfate will not only reduce calcium sulfate scale formation, but may also improve product water quality.

In general, this study has shown that there is no benefit to running at a low pH. Furthermore, there is no benefit to running at a high salt concentration except in terms of flux. Operating at a lower salt concentration would result in lower power consumption and process mass. Running at a lower salt concentration also means that the RO pressure would be lower due to the reduction in osmotic pressure, which is a benefit in terms of safety. The RO unit in the OD system was intended to run at 800 psi with 35 g/L of salt water.

CHAPTER EIGHT
FUTURE WORK

Based on the research conducted in this study, future work is necessary to understand the complete effect of feed pH on TOC rejection in osmotic distillation. This includes testing additional pH values to determine if there is a defined point at which the increase in TOC of the osmotic agent occurs, or if it is a gradual change from a feed pH of 3 to 7. Furthermore, in order to determine the effect of osmotic agent concentration on TOC rejection, several repeated runs will be necessary with improvements in accuracy. A different range of salt concentrations also may be required in order to observe an effect on TOC rejection. Lastly, the research in this study needs to be repeated using real urine in the feed; this may provide different results compared to the data collected using the transit mission wastewater ersatz. Typically product TOC concentrations are much lower when using real urine rather than simulated urine.

Several future experiments related to the work that was conducted in this study will determine the influence of the potential parameters that influence osmotic distillation performance in terms of TOC rejection. The five main tasks that need to be completed in order to obtain a better understanding of the osmotic distillation technology are listed below:

Task 1: Effect of pH and osmotic agent (a direct continuation of this hypothesis work):

The hypothesis studied is again that osmotic agent concentration and pH affect TOC rejection in osmotic distillation. Repeated runs will be conducted for feed pH values of 3, 7, and 10, and the osmotic agent concentrations of 20, 30, and 40 g/L (NaCl in water). Changes will be made to improve the accuracy and expand data generation quantities. The results from this data will verify the effect of the ionic strength of the osmotic agent. The focus of this research will be on generating more data as well as better statistical data for each run that was conducted.

Task 2: Effect of different osmotic agents and the pH of osmotic agent:

Selection of an osmotic agent and osmotic agent pH may have an effect on TOC rejection. To determine the influence of the osmotic agent, experiments will be conducted using various osmotic agents including a buffer. The osmotic agent for the first test will be NaCl with a concentration of 35 g/L or an osmotic pressure of approximately 400 psi. The osmotic agent for the second test will be a buffer; this buffer will be prepared using monobasic potassium phosphate (KH_2PO_4) combined with potassium hydroxide (KOH) at a pH of 7.21. The pH value of 7.21 was chosen due to pH limitations of the membrane and the three pK_a values of phosphoric acid which are 2.16, 7.21, and 12.32. In addition, the concentrations for the acid (KH_2PO_4) and base (KOH) are based upon the requirement of having an osmotic pressure of approximately 400 psi. The osmotic agent for the last three tests will be NaCl with a concentration of 35 g/L, and with pH values of 3.0, 7.21, and 10; the pH will be adjusted by adding either monobasic potassium phosphate or potassium hydroxide.

Task 3: Effect of temperature of the feed:

Temperature may have an effect on TOC rejection. To determine the effect of temperature, experiments will be conducted at different feed temperatures. The temperature values studied will be room temperature, 25 °C and 35 °C (maximum shell side temperature is 40 °C).

Task 4: Effect of flow rate and concentration polarization:

Flow rate and concentration polarization have an effect on TOC rejection. The effect of concentration polarization will be shown by running several tests with varying feed flow rates. Varying the feed flow rate will result in different flow regimes (laminar or turbulent) on the membrane, which disrupts concentration polarization. The various flow rates or the corresponding dynamic pressures of the feed studied will be 5 psig, 15 psig, 40 psig and 65 psig (maximum shell side pressure is 75 psig). The flow rates generated at these pressures will be determined by collecting the returning liquid in the feed stream over a specific time interval.

Task 5: Effect of using various membranes:

Lastly, membrane characteristics may effect TOC rejection. Therefore, different membranes will be tested, which will show the effect of membrane geometry/design (pore tortuosity, capillary pressure, contact angle, surface tension and pore radius) and membrane material on TOC rejection. The membranes that will be tested include selected microfiltration membranes with dissimilar membrane characteristics. The two membranes currently identified are made by Liqui-cel^{TM} and *Microdyn* -Nadir GmbH^{TM}.

CHAPTER NINE
CONCLUSIONS

The mechanisms that effect osmotic distillation are complex. In order to optimize the performance of OD membranes, it is important to understand the mechanisms that occur in osmotic distillation. The hypothesis for this study was that osmotic agent concentration and feed pH influence TOC rejection in osmotic distillation. The objective of this study was to determine the effect of the ionic strength of the osmotic agent and pH of the feed solution on total organic carbon rejection in osmotic distillation. The feed pH values studied include 3, 7, and 10, and the osmotic agent concentrations studied were 20, 30, and 40 g/L (NaCl in water). The results of this research indicated that feed pH had an effect on TOC rejection in osmotic distillation. The experiments using a feed pH value of 3 resulted in significantly higher TOC concentrations in the osmotic agent when compared to pH 7 and pH 10 experiments. Additionally, there was little or no difference in the TOC rejection values between the experiments with a feed pH of 7 and a feed pH of 10. The results also showed that osmotic agent concentration statistically has no effect on TOC rejection. Therefore, part of the hypothesis was verified true with respect to pH and part untrue regarding the effect of osmotic agent concentration on TOC rejection.

Based on the literature review conducted, the research in this study is rather unique and cannot be directly compared to previous studies. The lack of relevant research is the reason that this study was focused on the quality of the extracted water or TOC rejection. This aspect is what distinguishes this OD system from others and is what makes this research unique and significant. The results from this study contribute to further understanding of osmotic distillation by demonstrating the effect of ionic strength of the osmotic agent and the effect of pH of the feed on total organic carbon rejection.

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APPENDIX: RAW DATA

	Run time	**Volume (mL)**		**Production Rate**	**Recovery**	**pH (feed)**	**Conductivity of OA**	**TOC (ppm)**			
	Hrs	Feed	Product	(mL/hr)	%		IN (mS/cm)	Feed	Product	OA (persulfate method)	OA (combustion method)
pH = 3, OA = 20 g/L	0.000	7975	0		0.0%	2.80	18.55	1909			
	1.033	7975	150	145.2	1.9%	2.76	34.67				
	1.717	7950	260	161.0	3.3%	2.73	37.44	1744	55.20	101	110
	19.300	7925	1340	61.4	16.9%	2.86	34.63	2061	110.00	124	130
	20.850	7925	1420	51.6	17.9%	2.86	34.59				
	23.533	7925	1560	52.2	19.7%	2.87	34.58				
	23.733	7925	1570	50.0	19.8%	2.87	34.52		68.00		
	23.833	7925	1575	50.0	19.9%	2.87	34.76				
	26.150	7925	1685	47.5	21.3%	2.89	34.5				
	26.650	7900	1710	50.0	21.6%	2.90	34.59	2196	114.00	124	130
	44.767	7875	2120	22.6	26.9%	2.93	36.65	2454	67.90	128	140
	46.883	7875	2210	42.5	28.1%	2.93	35.72				
	47.500	7875	2235	40.5	28.4%	2.93	35.55		113.00		
	49.300	7850	2305	38.9	29.4%	2.93	34.95	2784	107.00	133	130
pH = 7, OA = 30 g/L	0.000	7975	0		0.0%	6.91	36.22	1913			
	0.317	7975	70	221.1	0.9%	6.87	39.81				
	0.617	7975	120	166.7	1.5%	6.82	47.56				
	1.600	7975	270	152.5	3.4%	6.95	56				
	2.333	7975	350	109.1	4.4%	6.93	56.28				
	2.650	7950	375	78.9	4.7%	6.92	55.76	1762	62.80	53.5	63
	20.333	7925	2125	99.0	26.8%	6.64	54.27	2207	67.90	62.2	67
	23.967	7925	2485	99.1	31.4%	7.02	54.3				
	25.317	7925	2615	96.3	33.0%	6.97	54.33				
	25.517	7925	2640	125.0	33.3%	6.95	54.27		68.80		
	26.800	7925	2760	93.5	34.8%	6.95	54.59				
	27.067	7900	2785	93.7	35.3%	6.93	54.2	2426	67.90	60.9	72
	43.833	7900	4335	92.4	54.9%	7.11	54.21		113.00		
	44.067	7875	4360	107.1	55.4%	7.12	54.34	3278	65.30	59.8	74
pH =10, OA = 30 g/L	0.000	7975	0		0.0%	10.03	35.32	1898			
	0.517	7975	100	193.5	1.3%	10.00	44.62				
	1.267	7975	130	40.0	1.6%	9.96	45.73				
	1.433	7950	150	120.0	1.9%	9.95	48.38				
	1.550	7950	175	214.3	2.2%	9.85	52.12	1801	63.70		61
	17.383	7925	1975	113.7	24.9%	9.85	54.56	2158	51.80	61.8	68
	18.067	7925	2045	102.4	25.8%	9.85	54.6				
	18.283	7925	2070	115.4	26.1%	9.85	54.64		75.30		
	21.600	7925	2413	103.4	30.4%	9.85	54.65				
	21.817	7925	2438	115.4	30.8%	9.85	54.45		66.50		
	24.117	7925	2678	104.3	33.8%	9.84	54.89				
	24.383	7900	2703	93.7	34.2%	9.84	54.46		67.80	57.8	67
	41.683	7900	4353	95.4	55.1%	9.79	54.74		69.00		
	41.983	7875	4378	83.3	55.6%	9.79	54.77	3389	68.70	66.3	73
	43.083	7875	4458	72.7	56.6%	9.80	54.75				
	44.217	7875	4548	79.4	57.8%	9.80	54.75				
	44.567	7850	4573	71.4	58.3%	9.80	54.69	3668	68.10	61.3	72
pH =10, OA = 40 g/L	0.000	7975	0		0.0%	9.81	42.52	1931			
	0.467	7975	50	107.1	0.6%	9.78	54.02				
	0.617	7975	100	333.3	1.3%	9.99	58.69				
	1.150	7975	190	168.8	2.4%	9.97	68.42				
	2.433	7975	360	132.5	4.5%	9.94	68.51				
	2.633	7950	385	125.0	4.8%			1837	55.10	44.7	54
	19.650	7950	2885	146.9	36.3%	9.90	68.1		28.40		
	19.833	7925	2910	136.4	36.7%	9.89	68.14	2383	55.00	47.1	63
	22.717	7925	3245	116.2	40.9%	9.89	68.03				
	22.933	7925	3270	115.4	41.3%	9.89	68.05		54.50		
	25.450	7925	3565	117.2	45.0%	9.88	68.09				
	25.650	7925	3590	125.0	45.3%	9.88	68.19		59.40		
	26.350	7925	3670	114.3	46.3%	9.88	68.29				
	26.567	7900	3695	115.4	46.8%	9.88	68.03	2729	28.80	51.3	62
	43.200	7875	5454	105.8	69.3%	9.78	68.05		62.40		
	43.417	7875	5479	115.4	69.6%	9.78	67.95	3972	46.60	52	64
	44.467	7875	5589	104.8	71.0%	9.78	67.87				
	45.833	7875	5739	109.8	72.9%	9.77	68.26				
	46.167	7850	5764	75.0	73.4%	9.77	68	4205	62.50	53.9	69

	Run time	Volume (mL)		Production Rate	Recovery	pH (feed)	Conductivity of OA	TOC (ppm)			
	Hrs	Feed	Product	(mL/hr)	%		IN (mS/cm)	Feed	Product	OA (persulfate method)	OA (combustion method)
pH =7, OA = 40 g/L	0.000	7975	0		0.0%	7.01	47.3	1910			
	0.033	7975	45	1350.0	0.6%	7.01	44.57				
	0.717	7975	155	161.0	1.9%	7.01	64.25				
	0.800	7950	180	300.0	2.3%	7.01	66.21	1875	56.80	41.6	52
	17.000	7950	2680	154.3	33.7%	6.99	69.65		52.80		
	17.167	7925	2705	150.0	34.1%	6.99	69.08	2313	27.30		62
	18.050	7925	2815	124.5	35.5%	6.98	69				
	21.067	7925	3195	126.0	40.3%	6.81	69.08				
	21.233	7925	3220	150.0	40.6%	6.80	69.07		54.90		
	22.683	7925	3410	131.0	43.0%	6.76	69.27				
	23.400	7900	3505	132.6	44.4%	7.17	69.14	2641	30.80	51.3	64
	24.017	7900	3585	129.7	45.4%	7.12	69.02				
	24.200	7900	3610	136.4	45.7%	7.11	69.16		65.40		
	41.900	7900	5860	127.1	74.2%	6.86	68.92		53.80		
	42.117	7875	5885	115.4	74.7%	6.89	68.86	4087	50.20	47.5	57
	43.083	7875	5995	113.8	76.1%	6.92	69.24				
	43.300	7875	6020	115.4	76.4%	7.00	69.73	4227	50.60	45.7	52
	45.617	7875	6160	60.4	78.2%	7.06	68.98				
	45.850	7850	6185	107.1	78.8%	7.06	69.01	4341	37.50	39	44
pH =10, OA = 20 g/L	0.000	7975	0		0.0%	9.83	21.97	1949			
	0.050	7975	80	1600.0	1.0%	9.83	22.66				
	0.350	7975	90	33.3	1.1%	10.05	34.85				
	0.550	7975	115	125.0	1.4%	10.04	34.58		45.20		
	2.667	7975	195	37.8	2.4%	9.99	34.57				
	3.450	7950	220	31.9	2.8%	9.98	34.71	1735	52.60	56.7	63
	20.083	7950	1220	60.1	15.3%	9.93	34.4		57.70		
	20.500	7925	1245	60.0	15.7%	9.93	34.68	2056	57.80	61.6	68
	23.117	7925	1395	57.3	17.6%	9.93	34.5				
	23.500	7925	1415	52.2	17.9%	9.93	34.57				
	23.933	7925	1440	57.7	18.2%	9.93	34.53		56.70		
	24.867	7925	1495	58.9	18.9%	9.93	34.49				
	25.283	7900	1520	60.0	19.2%	9.93	34.5	2111	66.50	62	70
	43.350	7900	2534	56.1	32.1%	9.89	34.79		58.30		
	43.850	7875	2559	50.0	32.5%	9.89	34.82	2481	62.00	66.6	70
	45.300	7875	2629	48.3	33.4%	9.90	34.43				
	45.750	7875	2651	48.9	33.7%	9.90	34.99				
	46.233	7850	2676	51.7	34.1%	9.90	34.6	2585	56.00	65.4	71
pH =7, OA = 20 g/L	0.000	7975	0		0.0%	7.18	20.84				
	0.150	7975	25	166.7	0.3%	7.18	27.85		32.00		
	0.967	7950	147.5	150.0	1.9%	7.17	34.87	1728	44.00	43.2	58
	1.467	7950	147.5	0.0	1.9%	7.16	34.96				
	17.000	7950	1047.5	57.9	13.2%	7.06	34.21		65.00		
	17.400	7925	1072.5	62.5	13.5%	7.03	34.63	2029	67.30	54.3	67
	20.217	7925	1232.5	56.8	15.6%	6.90	34.24				
	20.650	7925	1257.5	57.7	15.9%	6.88	34.73		65.00		
	23.750	7925	1607.5	112.9	20.3%	6.84	34.61				
	24.167	7900	1632.5	60.0	20.7%	6.84	34.41	2132	65.60	52.6	63
	41.450	7900	2702.5	61.9	34.2%	6.99	34.67		68.70		
	41.900	7875	2727.5	55.6	34.6%	6.97	34.51	2459	66.30	58	64
	44.400	7875	2867.5	56.0	36.4%	6.83	34.45				
	44.867	7875	2892.5	53.6	36.7%	6.81	34.37		69.80		
	46.517	7875	2982.5	54.5	37.9%	6.85	34.46				
	46.950	7850	3007.5	57.7	38.3%	6.87	34.46	2574	70.00	63.3	76
pH =3, OA = 30 g/L	0.000	7975	20		0.3%	2.79	31.61	1972			
	0.317	7975	50	94.7	0.6%	2.77	46.65				
	0.867	7975	163	205.5	2.0%	2.82	55.4				
	1.000	7950	188	187.5	2.4%	2.82	55.57		61.30		
	1.383	7950	238	130.4	3.0%	2.82	56.53				
	1.567	7950	263	136.4	3.3%	2.82	55.91	1849	67.40	54.7	86
	18.133	7950	2673	145.5	33.6%	2.84	55.2		97.40		
	18.333	7925	2698	125.0	34.0%	2.85	55.21	1965	97.40	80.1	110
	22.417	7925	3208	124.9	40.5%	2.86	55.39				
	22.533	7925	3233	214.3	40.8%	2.86	55.68		99.00		
	22.917	7925	3323	234.8	41.9%	2.86	56.24				
	23.117	7925	3348	125.0	42.2%	2.86	55.75		98.40		
	25.417	7925	4238	387.0	53.5%	2.86	55.41				
	25.617	7900	4263	125.0	54.0%	2.86	55.31	2904	97.00	83.9	120
	42.867	7900	6084	105.6	77.0%	2.87	55.34		98.80		
	43.167	7875	6109	83.3	77.6%	2.87	55.35	4629	103.00	86.9	120
	43.850	7875	6159	73.2	78.2%	2.87	55.25				
	44.133	7875	6184	88.2	78.5%	2.87	55.33		103.00		
	45.583	7875	6344	110.3	80.6%	2.87	55.35				
	45.933	7850	6369	71.4	81.1%	2.87	55.3	5103	103.00	87.6	120

	Run time	**Volume (mL)**		**Production Rate**	**Recovery**	**pH (feed)**	**Conductivity of OA**	**TOC (ppm)**			
	Hrs	Feed	Product	(mL/hr)	%		IN (mS/cm)	Feed	Product	OA (persulfate method)	OA (combustion method)
pH =3, OA = 40 g/L	0.000	7975	0		0.0%	3.12	42.17	1982			
	0.633	7975	130	205.3	1.6%	3.11	57.72				
	0.717	7950	155	300.0	1.9%	3.11	59.3	1807	62.70	43.4	73
	1.383	7950	175	30.0	2.2%	2.94	71.78				
	17.533	7950	3325	195.0	41.8%	2.94	71.4		89.50		
	17.633	7925	3350	250.0	42.3%	2.91	72.3	2868	90.60	68.1	110
	18.050	7925	3500	360.0	44.2%	2.91	73.93				
	18.167	7925	3525	214.3	44.5%	2.91	73.33		89.50		
	19.017	7925	3675	176.5	46.4%	2.91	71.22				
	19.133	7925	3700	214.3	46.7%	2.91	71.28		95.00		
	21.567	7925	4140	180.8	52.2%	2.92	71.27				
	21.700	7925	4165	187.5	52.6%	2.92	71.27		93.70		
	22.100	7925	4235	175.0	53.4%	2.93	71.06				
	24.333	7925	4615	170.1	58.2%	2.94	71.26				
	24.467	7900	4640	187.5	58.7%	2.94	71.1	3631	92.60	69.5	120
	27.017	7900	4666	10.2	59.1%	2.95	71.74				
	27.183	7875	4691	150.0	59.6%	2.95	71.75	4162	90.20	72.2	120
	29.467	7875	5051	157.7	64.1%	2.96	71.14				
	30.317	7875	5181	152.9	65.8%	2.96	71.11				
	30.483	7850	5206	150.0	66.3%	2.96	71.56	4794	86.00	69.3	110
pH =3, OA = 20 g/L	0.000	7975	0	170.8	0.0%	2.97	21.54	2000			
	0.467	7975	105	225.0	1.3%	2.93	35.72				
	1.133	7950	124	28.5	1.6%	2.92	34.63	2700	49.00		91
	18.917	7950	1124	56.2	14.1%	2.98	34.31		96.00		
	19.333	7950	1149	60.0	14.5%	2.98	34.44		100.00		110
	22.250	7950	1319	58.3	16.6%	2.97	34.53				
	22.683	7950	1344	57.7	16.9%	2.97	34.22		99.00		
	25.183	7950	1494	60.0	18.8%	2.96	34.41				
	25.583	7925	1519	62.5	19.2%	2.96	34.36		100.00		110
	43.083	7925	2480	54.9	31.3%	2.96	34.3		110.00		
	43.567	7900	2505	51.7	31.7%	2.96	34.21		100.00		130
	46.100	7900	2628	48.6	33.3%	2.96	34.16				
	46.617	7875	2653	48.4	33.7%	2.97	34.21	1900	100.00		120
	49.300	7875	2778	46.6	35.3%	2.98	34.38				
pH =3, OA = 40 g/L	0.000	7975	0	56.3	0.0%	3.00	37.57	2100			
	0.550	7975	170	309.1	2.1%	2.98	61.65				
	0.600	7950	195	500.0	2.5%	2.98	63.21				78
	15.083	7950	2895	186.4	36.4%	2.97	70.5				
	15.200	7950	2920	214.3	36.7%	2.97	70.37				110
	17.733	7950	3370	177.6	42.4%	2.99	70.67				
	18.183	7950	3450	177.8	43.4%	2.99	70.58				
	20.683	7950	3890	176.0	48.9%	3.01	70.56				
	20.817	7925	3915	187.5	49.4%	3.01	70.36				110
	34.983	7900	6065	151.8	76.8%	3.12	70.3				
	35.167	7900	6090	136.4	77.1%	3.13	70.57				110
	37.483	7900	6365	118.7	80.6%	3.17	70.4				
	37.633	7875	6390	166.7	81.1%	3.17	70.64	6600			99
pH =3, OA = 40 g/L	0.000	7975	0		0.0%	2.92	42.96	2100			
	0.700	7975	170	242.9	2.1%	2.92	61.3				
	0.767	7950	195	375.0	2.5%	2.92	64.14				84
	13.617	7950	2545	182.9	32.0%	2.91	70.68				
	13.750	7925	2570	187.5	32.4%	2.91	70.93				110
	17.300	7925	3170	169.0	40.0%	2.92	71.18				
	17.467	7925	3195	150.0	40.3%	2.92	70.65				
	19.933	7925	3595	162.2	45.4%	2.92	70.85				
	20.067	7900	3620	187.5	45.8%	2.92	70.89				110
	34.883	7900	5780	145.8	73.2%	2.91	70.83				
	35.083	7875	5805	125.0	73.7%	2.91	70.99				99
	37.183	7875	6045	114.3	76.8%	2.90	71.15				
	37.967	7875	6135	114.9	77.9%	2.90	70.72				
	38.167	7850	6160	125.0	78.5%	2.90	70.79	6600			89
pH = 3, OA = 20 g/L	0.000	7975	0		0.0%	2.87	24.45	2100			
	0.383	7975	60	156.5	0.8%	2.86	34.22				
	0.467	7950	85	300.0	1.1%	2.86	34.9	1650	43.20	84.88	75
	18.150	7950	1164	61.0	14.6%	2.90	34.27				
	18.550	7925	1189	62.5	15.0%	2.90	34.43	1988		106.6	100
	20.783	7925	1309	53.7	16.5%	2.91	34.27				
	24.867	7925	1536	55.6	19.4%	2.91	34.43				
	25.300	7900	1561	57.7	19.8%	2.91	34.11	2071	74.90	109.8	110
	42.250	7900	2495	55.1	31.6%	2.94	34.82				
	42.700	7875	2520	55.6	32.0%	2.94	34.21		66.20	97.97	94
	47.817	7875	2790	52.8	35.4%	2.95	34.38				
	48.267	7850	2815	55.6	35.9%	2.94	34.65	2900	63.80	93.95	90