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ISS Wastewater Pretreatment via DNA Pattern Picofilter Using Inorganic Brine Simulant

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Astronauts in the International Space Station (ISS) need as much water as they can access, whether it comes from people's breath, sweat or urine, recycled shower water or hand washing. It is of vital importance that any type of water is recycled and filtrated through different methods so it can be re-used. Recently, Cerahelix Inc. offered a ceramic tubular membrane element that uses DNA strands as a pattern in a sol-gel process that allows the sintered product to have a pore size in the picometer scale and claims to achieve ten times higher purity than other commercially available ceramic filters. This should allow higher purities and yields at reduced energy costs and theoretically allow near total dewatering of the reject stream and greater than 80% removal of polyvalent ions. Trials were performed with Cerahelix Inc. filters using an inorganic brine simulant at two pHs to test the efficiency of PicoHelix™ membranes and determine their feasibility for spacecraft wastewater treatment processes. Emphasis was placed on the polyvalent ions: SO_4^{2-}, PO_4^{3-}, Mg^{2+}, and Ca^{2+}. These ions should be rejected almost entirely from the feed solution and, not permeate through the filter. Results show that at a pH of 4.2, permeation of the polyvalent ions varied from 59% to 74% and at pH of 8.0, permeation varied from 72% to 87%. An Extended Nernst Planck (ENP) approach that describes the mass transfer process for a pico-filtration membrane was used to construct a model to inform the experimental expectations and outcome.

Nomenclature

ΔP = pressure difference
ACS = American Chemical Society
DSPM = Donnan steric partitioning pore model
ECLSS = Environmental Control and Life Support System
ENP = Extended Nernst Planck
ESM = equivalent system mass
FORO = forward osmosis-reverse osmosis
IC = ion chromatography
ID = inner diameter
ISS = International Space Station
KSC = Kennedy Space Center
NASA = National Aeronautics and Space Administration

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OD = outer diameter
RO = reverse osmosis
TRL = technology readiness level
V = brine solution velocity
VCD = vapor compression distillation

I. Introduction

ASTRONAUTS in the International Space Station (ISS) need water for the same reasons we need it here on earth. On earth, water is under a penny a liter, while in space this cost is dominated by launch costs where a liter of water can be more than $22,000. This cost increases markedly to lift water to the Moon or Mars, making recycling it a necessity. One of the major Environmental Control and Life Support System (ECLSS) practices on the ISS is water recovery from humidity, hygiene water, human urine, and eventually from laundry and hydroponics.

Modern ECLSS approaches use various separation processes to remove and purify the water from the influent wastewater while minimizing equivalent system mass (ESM).[1] On ISS in 2019, vapor compression distillation (VCD) is utilized to produce potable water via phase change at very high-energy efficiency.[2] Membrane technologies such as Reverse Osmosis (RO) and Forward Osmosis-Reverse Osmosis (FORO) have also been considered to lower ESM but so far are not as reliable and have a substantial energy cost.[3] Biological Life Support Systems are being considered for deep space exploration and bioreactors have been considered as green pretreatments to remove nitrogen.[4-7] These architectures offer the advantage of recapturing nutrients for food production. Nonetheless, a common problem for membrane separation processes is the susceptibility of the surface to fouling with polyvalent (having a charge of +/- 2 or more) ions such as Calcium, Magnesium, Sulfate, Phosphate, or Chromate. Membrane separation processes can effectively reject non-water ions but the solubility point of the remaining ions limits water recovery and terminal water recovery. A process prior to VCD or RO that effectively rejects polyvalent ions and allows monovalent salts (sodium and potassium chloride) and water to permeate through would allow for more complete, reliable, and efficient terminal water recovery.

Historically nano-filtration membranes have not shown the performance or efficiency to allow this separation.[3, 8, 9] Recently Cerahelix Inc. (Bangor, Maine) has offered a ceramic tubular membrane element that uses DNA strands as a pattern in a sol-gel process that allows the sintered product to have a pore size in the picometer scale (hence Picofiltration). Pore size can be controlled by using single stranded or double stranded DNA and RNA patterns during manufacturing. Cerahelix Inc. claims to achieve higher purity than other commercially available ceramic filters.[10] The pores should not have solubility limits that thin film processes and be more resistant to fouling, due to high shear rates, allowing higher purities and yields at reduced energy costs. Theoretically, this would allow near total dewatering of the retentate stream and greater than 80% polyvalent ion removal. Here we report the results of a series of tests performed in partnership with Cerahelix Inc. The goal was to test and validate the PicoHelix$^{\text{TM}}$ membrane for polyvalent ion removal under simulated conditions.

II. Materials and Equipment

A. Inorganic Brine Solution Preparation

ACS certified and graded reagents were purchased from Fisher Scientific or Sigma Aldrich and used to prepare all feed solutions. Table 1 shows a list of chemicals used along with the batch amounts. Nano-pure 18.2 MΩ water at 293 K from Labconco Water Pro BT Purification System was used as a solvent for the solutions. Initially, samples of different solutions prepared at different times were taken and then diluted between 10 to 10,000 times for ion chromatography (IC) analysis. The analysis was performed to determine concentrations of sodium, chloride, potassium, magnesium, ammonium, calcium, phosphate, and sulfate ions.

Inorganic Ersatz brine was chosen as a good starting point for testing after discussions with the Johnson Space Center.[11] Organics could be added to the brine to increase testing stringency in later tests if needed. A total of 10 L of brine solution were prepared and shipped for the initial testing at Cerahelix Inc. Of the 10 L, 5 L were used “as is” with a pH of 4.2, while the other 5 L were adjusted to a pH of 8.0 using 1.0 M sodium hydroxide solution. An Accumet AR50 Dual Channel pH/Ion/Conductivity meter from Fisher Scientific was used to measure the pH. The solutions were packed in boxes with frozen packets to keep the solutions cool and shipped overnight to Cerahelix Inc. in Maine.

Table 1. **Microgravity-based Ersatz brine recipe.**

Compound	Chemical Formula	Amount (g/L)
Sodium Chloride	NaCl	4.88
Potassium Chloride	KCl	1.26
Potassium Monobasic Phosphate	KH_2PO_4	4.77
Magnesium Chloride Hexahydrate	$MgCl_2\cdot 6H_2O$	0.70
Ammonium Chloride	NH4Cl	2.89
Calcium Chloride	$CaCl_2$	0.64
Sodium Sulfate	Na_2SO_4	3.25

Reagents were shipped overnight to Cerahelix Inc., as dry chemicals for the second verification trials. Four bottles were prepared, each containing pre-weighed dry reagents to make 6 L of brine solution. Solutions were prepared at Cerahelix Inc. by mixing RO high purity water and adjusting the pH using nitric acid for the pH of 3.0 and sodium hydroxide for the pH of 9.0. A National Aeronautics and Space Administration (NASA), Kennedy Space Center (KSC) team scientist traveled to Cerahelix Inc. to prepare solutions and oversee verification testing.

B. Filtration and Sample Collection (Cerahelix Inc.)

Two trials were performed by Cerahelix Inc. The first trial used the premixed solutions that were stored at 10 °C upon arrival. The second trial used the dry chemical mixes that were shipped to Cerahelix Inc. and mixed on site.

Figure 1 shows the cross flow filtration system set up and the PicoHelix™ filters that are placed inside the filter housings. Initially 2 L of solution were circulated through the system to prime the filters and build up a charge layer on the membrane; this should increase the membrane specificity. The system was not pressurized during the priming process. For the tests, the priming solution was removed and the test was started with a fresh 2 L of feed. Solution passing through the filter (permeate) flows out through a tube at the top of the test stand and is collected. The retentate is recirculated to the feed tank. A 10 mL sample of the starting feed was taken at the beginning of the experiment. After one hour, the pressure was raised to 500 psig and a timer was set for 15 minutes. Permeate samples (10 mL) were collected every 15 minutes for the duration of the test. These samples were taken from the composite permeate at that time point using sterile centrifuge tubes and pipets. At the end of the tests, 10 mL samples of total composite, permeate, and retentate were also taken. Once the test was over and all the samples collected, they were refrigerated at 10 °C, and sent to NASA KSC for ion chromatography (IC) analysis.

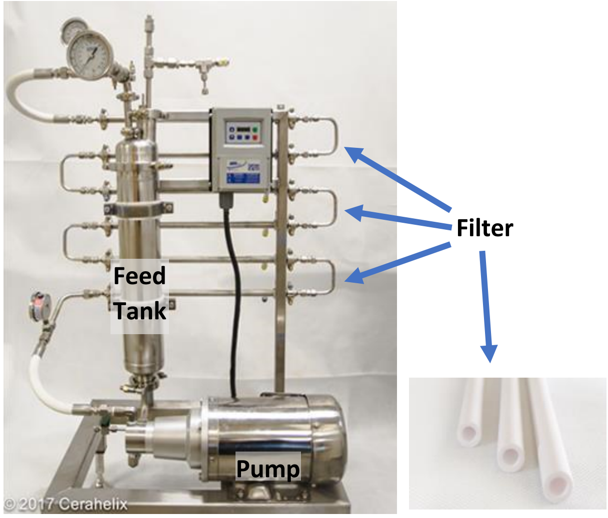

Figure 1. Cerahelix Inc. cross flow filtration system setup and PicoHelix™ filter.

A third trial using calcium-sulfate solution was done directly after the inorganic brine filtration. For this analysis, HACH® Sulfate TNT plus® 865 vial testing tubes were used. The initial concentration of calcium sulfate was 100 ppm.

Conductivity, pH, and temperature were recorded throughout all tests. A Thermo Scientific™ Orion Portable pH Meter was used to measure the pH directly after a sample was collected. Conductivity and temperature were measured using a Myron L® Company Ultrameter II™ 4P. These tests were also done directly after collecting the sample.

A chemically enhanced flush was performed for one hour after each trial to maintain the integrity of the membrane. The system was cleaned by filling the feed tank with a 0.1% Alconox and 0.25% citric acid solution and running it for 30 minutes, then flushing with ultrapure water.

C. Ion Chromatography

When the samples were received from Cerahelix Inc., they were stored at 10 °C. The samples were then prepared for IC analysis by making dilutions from 10 to 10,000 X to determine ion concentrations. Nano-pure 18.2 MΩ water from a Labconco Water Pro BT Purification System was used for the dilutions.

The Dionex ISC-3000 system was primed, flushed, and allowed to stabilize for a minimum of 30 minutes prior to each run. For these experiments, anions were evaluated using the Dionex AG18/AS18 column and potassium hydroxide eluent. Cations were evaluated using the Dionex CG12A/CS12A column and methanesulfonic acid eluent.

Both eluents were made using 18.2 MΩ water that has been degassed in an ultrasonic bath. Eluent flow rate was set to 1.0 lpm for both anions and cations. The methods used were based on EPA Method 300.[16] The instrument was calibrated using known dilutions of commercial standards at the following concentrations: 0.1, 0.25, 0.5, 0.75, 1.0, and 2.0 ppm. Two blank samples were run prior to each calibration. The Dionex 3000's internal software, Chromeleon, generated a linear calibration from these samples and the calibration curve was manually verified. Samples were diluted so that the concentrations of target ions fell within the 0.1 to 2.0 ppm calibrated range. Check standards were run prior to each set of runs to verify the current calibration. Blanks were run before and after the initial check standard. Additional check standards were run every 10 to 20 samples for data sets with numerous samples.

III. Results and Discussion

A. Brine Analysis via Ion Chromatography

Brine verification analysis was done to establish the reproducibility of the feed preparation before shipping any to Cerahelix Inc. All samples prepared were analyzed for Na^+, Cl^-, K^+, NH_4^+, SO_4^{2-}, PO_4^{3-}, Mg^{2+}, and Ca^{2+} ions. The concentration of each of the ions was then calculated based on the calibration curves previously prepared from IC standards. The mass of each ion present was calculated and compared to its theoretical value. The highest percent error (14% - 15%) was for NH_4^+, Mg^{2+}, and Ca^{2+} ions. All of these had starting amounts under 1000 mg/L. This data was compared to the feed sent to Cerahelix Inc. prior to filtration to validate protocols and measure sources of error.

B. Cerahelix Inc. Testing

1. Testing at a pH of 4.2 and a pH of 8.0

Cerahelix Inc. indicated the performance of the PicoHelix™ filter is ideal under acidic or basic pH but not at neutral pH. For the first two tests, 3 L of feed solution at either pH 4.2 or 8.0 were placed in the feed tank (Figure 1) and introduced at 0.64 and 0.58 lpm, respectively, into the system. Pressure and temperature were held at 500 psig and room temperature respectively. Samples were taken from the total composite permeate every 15 min for the duration of the test. Table 2 shows the original starting feed, and permeate volumes obtained before each sample was taken. The total mass of the ions were calculated using these volumes. The pH 4.2 test ran for 120 min, and the pH 8.0 test ran for 80 min. Both tests ran until 10% of the original volume remained in the feed tank. Sulfate was measured in the retentate portion, at the end of the test as a quick determination of the filter performance. No other retentate samples were collected as this required stopping the test and depressurizing the system to collect the sample.

Table 2. Permeate sample volumes before each time point collection.

Run	pH 4.2									pH 8.0					
Sample #	Feed	1	2	3	4	5	6	7	8	Feed	1	2	3	4	5
Volume (mL)	3000	472	862	1226	1570	1890	2190	2452	2700	2757	640	1162	1674	2214	2632

2. IC Sample Analysis for pH 4.2 and pH 8.0 Tests

Table 3 shows the total mass of each ion at a pH of 4.2. These masses were calculated based on the concentrations (mg/L) obtained from IC analysis and the volumes from Table 2 (mass = concentration (mg/L)*volume (L)).

Table 3. Calculated mass of each Ion at pH of 4.2.

	Ion Amount (mg)										
Ion	**Feed**	**Permeate**								**Composite**	**Retentate**
		0	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**	
Cl^-	18398.6	N/A	2258.8	4364.7	6339.4	7951.0	9582.3	11563.2	12700.1	14591.2	1849.9
SO_4^{2-}	7109.3	N/A	639.3	1474.6	1975.7	2276.2	2738.0	3235.8	3689.9	4166.4	1221.5
PO_4^{3-}	10427.7	N/A	1038.6	2361.7	3497.1	4490.6	4513.1	5243.4	5781.7	6700.4	1738.7
Na^+	10444.3	N/A	1105.0	1883.4	2636.5	3359.4	4139.6	4889.2	5690.3	7310.9	1583.7
NH_4^+	2828.2	N/A	323.3	622.4	903.9	1235.3	1379.9	1716.2	1790.3	2011.2	341.1
K^+	5576.9	N/A	654.3	1246.8	1800.8	2344.6	2786.0	3672.5	3720.4	4241.3	1121.4
Mg^{2+}	210.7	N/A	25.5	49.2	68.9	90.3	107.0	123.5	141.6	154.0	28.7
Ca^{2+}	568.1	N/A	66.3	129.8	179.9	235.3	281.6	326.4	377.1	422.6	80.4

Figure 2 shows all ions passing through the filter as a function of time with little or no discrimination between polyvalent, monovalent, cation or anions. The polyvalent ions studied were SO_4^{2-}, PO_4^{3-}, Mg^{2+}, and Ca^{2+}; these ions were expected to be retained in the feed solution and absent in the permeate. Of greater importance is that neither the concentration nor the ratio of concentrations of ions (e.g. $[Ca^{++}]/[K^+]$) changes much over the course of the run indicating that the pores are most likely too big to selectively filter ions.

The approach for the pH 8.0 test was slightly different as a result of a small errors performed by the Cerahelix Inc. team. The initial feed solution was not the expected 3000 mL, and the final collection happened at 80 minutes. Permeate samples were only collected for a total of one hour and fifteen minutes as the filter did not have the same performance as with acidic solutions. Table 4 shows the data for each of the ions already converted in milligrams at a pH of 8.0.

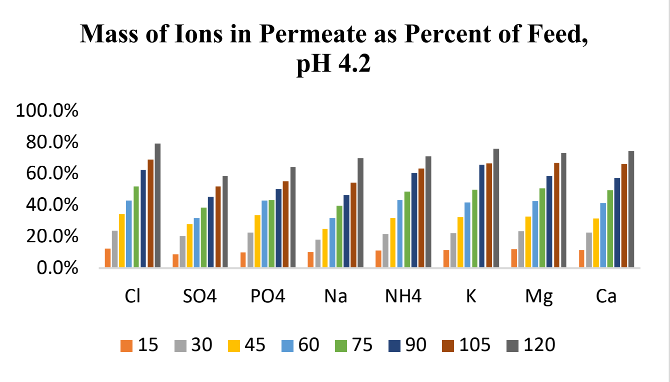

Figure 2. Percent of feed ions passing through the filter vs time with respect to the feed solution at a pH of 4.2.

Table 4. Calculated mass of the different ions at each time collection at pH of 8.0.

	Ion Amount (mg)								
Ion	**Feed**	**Permeate**						**Composite**	**Retentate**
		0	**15**	**30**	**45**	**60**	**75**	**80**	
Cl^-	16677.1	N/A	3443.0	6332.0	9173.2	12656.6	14930.7	23017.4	647.1
SO_4^{2-}	6465.8	N/A	1140.4	2218.4	3197.8	4684.6	5644.8	5387.8	296.5
PO_4^{3-}	7339.2	N/A	1304.7	2490.2	3653.7	5123.9	6191.4	6214.6	348.5
Na^+	28329.9	N/A	1975.0	3634.9	5360.6	7483.31	8658.4	8748.3	396.3
NH_4^+	2558.2	N/A	503.4	954.7	1394.2	1868.9	2252.4	2285.5	111.5
K^+	5150.1	N/A	1012.0	1947.9	2854.1	3792.4	4678.6	4678.4	255.1
Mg^{2+}	9.85	N/A	1.9	3.4	5.2	7.0	8.2	8.5	0.5
Ca^{2+}	16.2	N/A	4.6	5.0	7.2	9.9	11.7	11.6	0.7

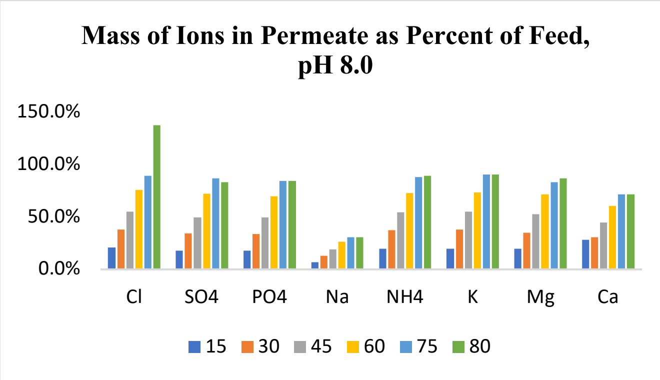

Figure 3. Percent of feed ions passing through the filter vs time with respect to the feed solution at a pH of 8.0.

The results at pH 8.0 were similar to those at pH 4.2. Once again, all polyvalent ions were observed to pass through the membrane and concentrations of each ion changed slightly over time (Figure 3). Ratios of one ion to another at each time point indicated that the filter was not highly selective for particular ions, e.g. the membrane was unable to effectively alter ion concentrations in either the permeate or the retentate. It should be noted that both Mg^{2+} and Ca^{2+} were essentially not present in the pH 8.0 feed solution. They should have been present at 84 mg/L and 280 mg/L respectively. Only 3-4% of these ions were present.

3. *Verification Test at pH 3.0 and pH 9.0*

Dry inorganic brine solution ingredients for a 6 L batches were prepared in advance and shipped to Cerahelix Inc.. On site, these dry ingredients were mixed with DI water in a volumetric flask, ensuring that all solids had fully dissolved. Several rinses were done in the bottle in which the dry chemicals were shipped to ensure that all material was captured in the 6 L final volume of the brine solution. Two 6 L batches were prepared and left to sit overnight. The solutions were stirred again the following morning followed by a pH adjustment for the upcoming tests. One batch was adjusted to a pH of 3.0 using nitric acid and the other was adjusted to a pH of 9.0 using sodium hydroxide. The pHs were more basic and more acidic than the previous test to improve the charge effects on the membrane during the filtration process with the hope that this would increase selectivity. Since all the ions are smaller than the filter's pore size, the filtration depends entirely on charge effects between the ions and the pores.

Prior to the start of each test, two liters of the pH-adjusted brine solution was added to the feed tank and circulated through the system for one hour to allow an ionic layer to build up, increasing the charge effects. This solution was then drained from the system and a fresh 3 L of the low pH-adjusted brine solution was added. Once the 3.0 pH test was completed the same procedure was repeated for the pH 9.0 feed solution.

Throughout the test, the total volume of solution passing through the filter was tracked. The parameters for testing were set at 3.3 lpm flow, 500 psig, and room temperature. Samples were collected from the permeate every 15 minutes for IC analysis. Samples were also collected from the retentate when 50%, 80%, and 90% of the total solution volume had passed through the filter. Cerahelix Inc. refers to those samples as 2x, 5x, and 10x samples because the solution remaining in the retentate would be 2x, 5x, and 10x more concentrated for materials not passing through the filter than its original amount. Table 5 shows the volumes before each sample was collected.

The test had to be stopped to depressurize the system to collect retentate samples. Because of this, retentate was only sampled at the 2x and 10x points; and at the end of the test. Prior to sampling the retentate, approximately 50 mL of solution was dispensed from a valve and dumped back into the feed tank twice in order to ensure that the sample was not impacted by any non-circulating solution trapped in the valve.

Table 5. Permeate sample volumes (mL) before each time point collection.

Run	pH 3.0					pH 9.0				
Sample #	Feed	1	2	3	4	Feed	1	2	3	4
Volume (mL)	2937	826	1671	2428	2681	2937	692	1392	2170	2817

4. *IC Sample Analysis for pH 3.0 and 9.0 Tests*

All of the samples were diluted prior to analysis to have concentrations within the IC calibrated range. Table 6 shows all data converted into milligrams of the corresponding ion at a pH of 3.0. As previously mentioned, all mass calculations were obtained after determining the concentration of the ion via IC and using the volumes at each time point from Table 5.

Table 6. Data of calculated mass of the different ions at each time of permeate collection, feed, and retentate at pH of 3.0.

	Ion Amount (mg)								
	Feed/Retentate			Permeate					
Ion	**0**	**26.5**	**50**	**0**	**15**	**30**	**45**	**50**	**10x**
Cl^-	21560.4	11655.7	1565.8	N/A	6270.7	12405.2	17388.6	20023.3	21957.7
SO_4^{2-}	0.0	0.0	0.0	N/A	0.0	0.0	0.0	0.0	0.0
NO^{3-}	559.3	277.9	33.8	N/A	152.4	304.0	421.4	481.1	496.1
PO_4^{3-}	8618.5	4859.4	718.4	N/A	2432.5	4777.7	6858.8	7905.1	8552.8
Na^+	8665.2	4842.2	644.5	N/A	2560.7	5098.5	7069.6	8125.6	8863.9
NH^{4+}	2993.3	1557.5	206.3	N/A	817.7	1632.1	2321.4	2363.3	2821.3
K^+	6037.0	3019.7	414.9	N/A	1636.9	3249.1	4549.4	4710.3	5693.7
Mg^{2+}	236.2	120.6	17.2	N/A	62.6	129.1	177.1	208.5	211.1
Ca^{2+}	651.2	332.2	45.2	N/A	201.9	361.1	566.3	611.2	657.7

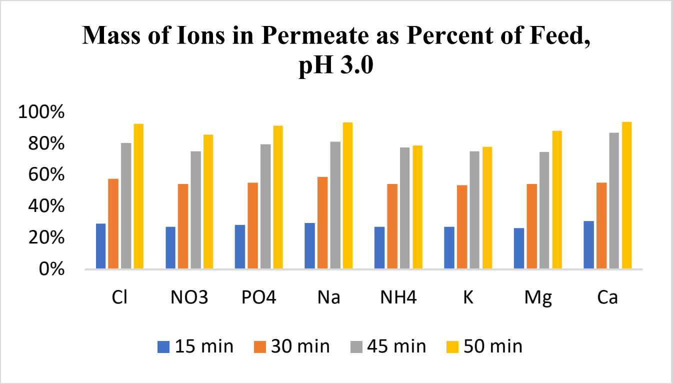

Figure 4. Percent of feed ions passing through the filter vs time with respect to the feed solution at a pH of 3.0.

Even though the target pH was reduced to 3.0 to enhance the charge effect on the membrane, the results were similar to the pH 4.0 test. The hope for results were that the polyvalent ions (SO_4^{2-}, PO_4^{3-}, Mg^{2+}, and Ca^{2+}) would be unable to pass through the membrane and remain in the retentate. All ions were passed through the membrane and concentrations of each ion changed slightly over time (Figure 4). Ratios of one ion to another at each time point indicate that the filter was unable to effectively alter ion concentrations in either the permeate or the retentate.

Sulfate is part of the brine mix, but was not detected by IC. We were unable to determine why these ions were missing.

Table 7. Calculated mass of the different ions at each time of collection at pH of 9.0.

	Ion Amount (mg)									
	Feed/Retentate			Permeate						
Ion	0	31	56	0	15	30	31	45	56	10x
Cl^-	22443	11193	1554.3	N/A	5186.4	11134	11324	17373	20055	20456
SO_4^{2-}	48.7	19.3	2.9	N/A	0.0	0.0	0.0	0.0	0.0	0.0
NO_3^-	0.0	0.0	0.0	N/A	0.0	0.0	0.0	0.0	0.0	0.0
PO_4^{3-}	7180.0	3657.8	522.7	N/A	1625.0	3493.0	3557.2	5350.1	6322.3	6425.5
Na^+	12253	6153.4	875.7	N/A	2889.3	6116.2	6056.5	9555.8	11363.2	10940.2
NH_4^+	2578.7	1278.5	184.5	N/A	576.9	1237.4	1271.2	1809.7	2315.4	2296.3
K^+	5789.0	2839.7	411.0	N/A	1341.0	2807.7	2878.7	4538.3	5291.5	5200.0
Mg^{2+}	X	X	X	N/A	X	X	X	X	X	X
Ca^{2+}	X	X	X	N/A	X	X	X	X	X	X

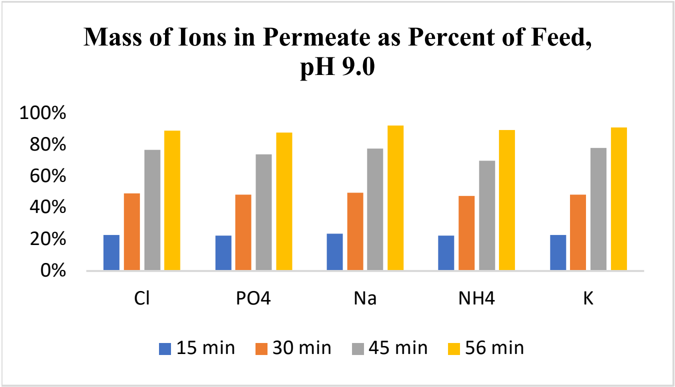

Figure 5. Percent of feed ions passing through the filter vs time with respect to the feed solution at a pH of 9.0.

As with the initial test, an alkaline pH trial was done to determine if there was any difference in the performance of the filter at a high pH. For this test, the pH was increased to pH of 9.0 from 8.0 based on recommendations from the Cerahelix Inc. team. Table 7 shows milligrams of the corresponding ion at a pH of 9.0 and Figure 5 shows the percentage of the feed ions moving through the filter over time.

The results at pH 9.0 were similar to all previous tests, with all ions passing through the membrane. The concentrations of ions remained the same over time indicating that the membrane was not selective, and did not present a barrier to their passage. Sulfate ions were notably absent from the brine mix as with the pH 3.0 test, raising the possibility that they were omitted from the mix.

Ca^{2+} and Mg^{2+} ions were also absent from the pH 9.0 test, similar to what was seen in the pH 8.0 test. Since these ions were seen in the pH 3.0 test, their absence cannot be easily explained as an omission as the dry reagents for both the pH 3.0 and 9.0 test were made at the same time.

C. Calcium Sulfate Test

Cerahelix Inc. had experience with calcium sulfate ($CaSO_4$) and suggested that their filters are effective for these ions; therefore, a final test was performed to ensure we understood the filters performance. Divalent ions of SO_4^{2-} and Ca^{2+} would be expected to remain in the retentate with only water passing through the filter (permeate).

A total of 3000 mL (100 mg/L) of calcium sulfate feed solution were introduced at 3.3 lpm at the same parameters used before; the same procedure was also followed. Permeate samples were taken every 15 minutes until 90% of the total solution went through the filter. Retentate samples were taken as in the previous two tests. Table 8 shows a summary of all the parameters of the permeate samples taken through an 80 minutes time. After all the samples were collected, they were sent to KSC for analysis (Table 9).

Table 8. Permeate sample volumes (mL) before each time point collection.

Run	Gypsum ($CaSO_4$)					
Sample #	Feed	1	2	3	4	5
Volume (mL)	3000	515	1089	1706	2256	2622

Table 9. Ion concentrations for calcium sulfate solution vs time.

	Ion Amount (ppm)									
	Feed/Retentate			**Permeate**						
Ions	**0**	**37**	**71**	**0**	**15**	**30**	**45**	**60**	**71**	**10x**
SO_4^{2-}	68.32	75.63	111.45	N/A	52.30	54.24	58.13	63.16	63.58	62.60
Ca^{2+}	22.97	27.46	41.03	N/A	17.19	17.54	19.06	21.80	21.10	21.45

The results of this test were consistent with all previous tests. Close to 80% of the ions went through the filter instead of remaining in the retentate. Figure 6 shows a breakdown of the permeate ions every 15 min; at 71 minutes (90% of feed went through) a total of 79% of SO_4^{2-} and 78% of Ca^{2+} made it through. The filter might be concentrating the polyvalent ions in the retentate at the final stages of the run, but not in a highly selective manner.

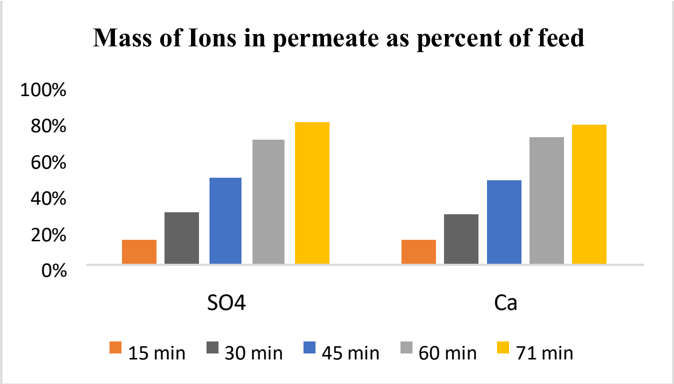

Figure 6. Percent of ions passing through the filter with respect to $CaSO_4$ feed solution.

D. Extended Nernst-Planck Approach for Pico-filtration Model Based on the Donnan Steric Partitioning Pore Model

To better understand how the filter should have performed, the authors built a mathematical model on pico-filtration describing the physical-based separation of ionic species present in the brine solution. The pico-filtration model is based on the Donnan Steric Partitioning Pore Model (DSPM) and is intended to obtain permeate composition as a function of feed composition and operating conditions. The model is suitable to describe the interaction between the pico-porous membrane and the multi-ionic brine solution. The DSPM model uses the Extended Nernst-Planck (ENP) approach to describe ion transport inside the pico-pores under the effect of drag forces. In a one dimensional approach, the model averages the radial effects and considers only concentration gradients along the membrane thickness. At the membrane boundaries (feed and permeate side), ion partitioning between membrane and solution is defined by the steric-Donnan equilibrium. The model derives the concentration gradient from the combination of the ENP equation with the electron-neutrality condition. As the concentration gradient depends on permeate concentration, the model obtains the numerical solution via an iterative procedure integrating the concentration gradient using finite differences.

1. *Mathematical Formulation*

The DSPM considers that the solute and solvent transport takes place in cylindrical pores of known effective radius (r_p) and effective length (Δx). The membrane has an effective membrane charge (X_d). The pressure difference established between both membrane sides causes a solvent flow inside the pore of velocity (V) defined by the Hagen Poiseuille approach as illustrated in Equation 1.

$$V = \frac{\Delta P \, r_p^{\,2}}{8 \, \mu \, \Delta x} \tag{1}$$

Where V is the brine solution velocity (m/s), ΔP is the pressure difference (N/m^2), μ is the dynamic viscosity of the brine solution (kg.m/s), Δx is the effective membrane length (m), and r_p is the effective membrane radius (m).

Convection, diffusion and electrical forces are the driving forces to yield a solute flux (J_i) through the membrane. The model calculates individual solute transport via the ENP approach as illustrated in Equation 2.

$$J_i = -K_{i,d} \, D_{i,\infty} \frac{d c_i}{d x} + K_{i,c} \, c_i \, V - z_i \, c_i \, K_{i,d} \, D_{i,\infty} \frac{F}{R_G T} \frac{d \Psi_m}{d x} \tag{2}$$

Where J_i is the flux ($mol/m^2/s$) of ion solute i, C_i is the concentration (mol/m^3) of ion solute i, Ψ_m is the electrical potential in the membrane (V) , $K_{i,d}$ is the ion diffusive hindrance factor (-) of ion solute i , $K_{i,c}$ is the ion convective hindrance factor (--) of ion solute i, $D_{i,\infty}$ bulk is the bulk diffusion coefficient (m^2/s) of ion solute i , and Z_i is the solute ion charge (-) , and R_G is the gas constant (8.314 J·mol/K).

The ENP equation differs from the widely-used Nernst-Planck (EN) equation on the use of drag coefficients for convection ($K_{i,c}$) and diffusion ($K_{i,d}$). These coefficients correct the convective and diffusive transport in the bulk solution for a solute confined in a pore. The model uses the expressions found in the literature to calculate the drag coefficients as function of the membrane's pico-pore radius (r_p).[12]

The electron-neutrality conditions stated in equations 3, 4, and 5 must be fulfilled in the feed solution, membrane and permeate respectively. Besides, the compositions in the membrane at the feed wall are related to the solute compositions at the membrane via the Donnan steric-partitioning condition as stated in equation 6; and the same for the compositions in the membrane and permeate solution (equation 7). The steric-partitioning coefficient (Φi) used in these equations is calculated using below-mentioned ratio (λ_i) as stated in equation 8. These conditions must be fulfilled separately for each solute, but depend on the Donnan potential established at each membrane side.

$$\sum_i z_i\, C'_{i,f} = 0 \qquad (3)$$

$$\sum_i z_i\, c_i + X_d = 0 \qquad (4)$$

$$\sum_i z_i\, C_{i,p} = 0 \qquad (5)$$

$$\frac{\gamma_{i,0}\, c_{i,0}}{\gamma_i C'_{i,f}} = \Phi_i \exp\left(- \frac{z_i F}{R_G\, T} \Delta\Psi_D \Big|_{x=0} \right) \qquad (6)$$

$$\frac{\gamma_{i,\Delta x}\, c_{i,\Delta x}}{\gamma_{i,p} C_{i,p}} = \Phi_i \exp\left(- \frac{z_i F}{R_G\, T} \Delta\Psi_D \Big|_{x=\Delta x} \right) \qquad (7)$$

$$\Phi_i = \left| \begin{array}{ll} 1-\lambda_i^2 & \text{si } \lambda_i < 1 \\ 0 & \text{si } \lambda_i \geq 1 \end{array} \right. \qquad (8)$$

where $C'_{i,f}$ is the feed concentration of solute i, Φ_i is the steric coefficient of solute i, and λ_i is the ratio of the Stokes radius of the solute i to the effective pore radius.

Equations 6 and 7 define the boundary conditions at both membrane sides. In our case, ideal conditions is assumed, so the activity coefficients are set to one (1.0). The membrane properties used in the model include a membrane's pico-pore r_p = 0.5 nm (500 pm), an effective membrane charge X_p = 0 mol/m^3, and a ratio of the effective pore $\Delta x/Ak$ = 1 µm.

2. *Model Case: $CaSO_4$ Solution*

The mathematical description of the pico-filtration process formulated in equations 1 through 8 was used to build a one dimensional model in COMSOL® and simulate the $CaSO_4$ test experimentally conducted and its outcome documented in Figure 6 and Tables 8 and 9. Table 10 lists the properties for Ca^{2+} (i = 1) and SO_4^{2-} (i = 2) ions used in the model.

The additional properties of Ca^{2+} and SO_4^{2-} ions used in the model are dependent of the porous radius (r_p), calculated assuming r_p = 0.5 nm (500 pm), and listed in Table 11.

The inlet operating conditions used in the model as boundary conditions are those used in the $CaSO_4$ test summarized in Table 9 and include $CaSO_4$ composition of 100 mg/L (0.73 mol/m^3), flow rate of 3.3 lpm, temperature of 20 °C, and pressure of 500 psig (2,758 kPa). The inlet $CaSO_4$ solution flow of 3.3 lpm distributed into six membrane tubes having 3-mm inner diameter (ID) and 6-mm outer diameter (OD) leads to a solution bulk velocity of V = 0.013 m/s. Figure 7 shows the Ca^{2+}/SO_4^{2-} concentration profile along the membrane obtained by the pico-filtration model using an uncharged membrane (X_d = 0) at the experimental operating conditions stated above.

Table 10. Ion properties.

	Ca^{2+}	SO_4^{2-}
i	1	2
Z_i (-)	1.351	1.467
$D_{i,\infty}$ (m^2/s)	0.72x10^{-9}	1.06x10^{-9}
$r_{s,i}$ (nm)	0.357	0.231

Table 11. Ion properties calculated using r_p = 0.5 nm (500 pm).

	Ca^{2+}	SO_4^{2-}
i	1	2
$K_{i,c}$ (-)	1.351	1.467
$K_{i,c}$ (-)	0.0315	0.2055
Φ_i	0.0902	0.2894

As it can be seen, Ca^{2+}/SO_4^{2-} concentration at the bulk-membrane interface ($x/\Delta x = 0$) happens to be estimated by the model as 0.144 mol/m^3, lower than the feed bulk concentration (0.73 mol/m^3) because of the expected steric effect. The model forecasts a concentration value of 0.037 mol/m^3 at the opposite membrane's edge ($x/\Delta x = 1$) yielding 75% of local retention for both Ca^{2+} and SO_4^{2-} ions allowing 25% of them passing through the pico-porous membrane filter. This is essentially opposite of the experimental outcome that yielded 80% ion passage. A further parametric study on the model showed that getting 80% ions passing through requires setting undervalued ionic properties for both Ca^{2+} and SO_4^{2-}.

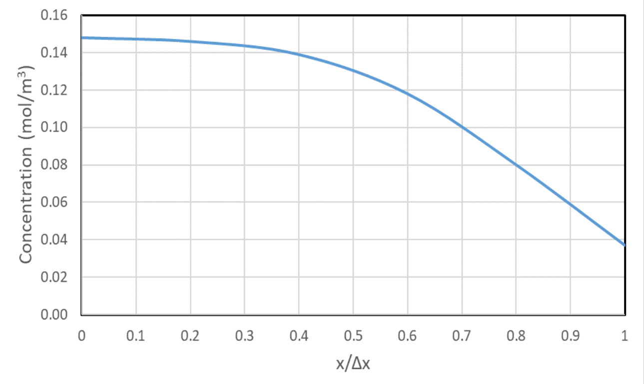

Figure 7. Ca^{2+}/SO_4^{2-} concentrations along the membrane thickness for $x_p = 0$.

The described model is for a t = 0 of the membrane operation of a batch process with full reject recycle, or t = 0 to infinity for a continuous process with no reject recycle. However, the influent stream used during the testing is continuously concentrated by the back-feed of the reject stream passing through the membrane (assuming ideal mixing). The water flux is higher than solute flux, the influent concentration increases over time. At early times in the experiment, the flux of monovalent/ divalent was high until concentration polarization and other phenomenon start to dominate at higher brine concentrations and the separation ceases to be effective (experiment is over once flux or flux ratio goes below a critical amount). This test should be able to show an ideal separation using a perfect membrane, and shows how the performance (such as peak flux ratio of certain salt pairs or terminal concentration ratio once flux is reduced to a certain level) degrades if the pore size is higher than expected. There were two variables at play: a defect size (pore larger than specified) and defect ratio (fraction of pores that are defect sized). The model suggests that there were at least a small fraction of larger pores that sharply reduced the monovalent/divalent characteristic separation.

IV. Conclusions

A. Filter Performance

The fundamental premise of the PicoHelix™ filter is that small pore sizes can be made using DNA or RNA. In principle this possible, however, when you look at the dimensions of DNA, its smallest dimension (its diameter) is 2000 pm, while the ionic radii of calcium, magnesium, sulfate, and phosphate are all under 300 pm. If the biggest pores in the filter were the diameter of a DNA double helix, then the pores would be on the order of eight times larger than the ionic radii. However, the actual pore size was not determined.

All tests showed that the PicoHelix™ filter did not meet the rigid requirements for removing polyvalent cations from a simulated ISS wastewater stream. The pressures and flows used in testing were selected by Cerahelix Inc. based on their experience. Had the filter performed well, the number of filters would have been increased (surface area) and the flow rates and pressures reduced to reduce energy demand. The pH 4.2 data suggests that there may have been 2X or more concentration of the sulfate, sodium, and potassium ions, however, this was not seen at pH 3.0 nor under alkaline conditions. There were substantial challenges in collecting, labeling, and handling of all the samples throughout all of the runs, but particularly during the first trials (pH 4.2 and pH 8.0). Even taking the pH 4.2 experiment at face value, doubling the concentration of sulfate, sodium, and potassium ions in the final 10% of the volume would have little effect on the wastewater stream. The impact on Ca^{2+} and Mg^{2+} was much smaller. There is greater importance in these ions due to their role in water hardness.

Biological membranes have highly selective ion channels that are made of proteins often having charged groups at one or both ends of the pores. The radii of these channels is tightly controlled allowing for highly selective ion channels. The PicoHelix™ filter did not approach this level of selectivity or sophistication, but as bio-fabrication techniques improve, there is hope that such a membrane can be manufactured cost effectively.

B. Removal of Calcium and Magnesium under Alkaline Conditions

It should not be surprising to find very little to no calcium and magnesium ions in the alkaline brine solutions, as a separate project was being run simultaneously on recovering phosphate by forming struvite ($(NH_4MgPO_4)\cdot 6H_2O$) from waste water streams. Daegi Kim *et al.*[13] describe optimal recovery of ammonia and phosphate from swine wastewater streams in the pH range from 8.0 to 11. Suller *et al.*[14] describe struvite precipitation in human urine at pH as low as 6.2. Calcium forms phosphate precipitates (like hydroxyapatite) under alkaline conditions that have poor solubility between pH 8 and pH 9.[15] Phosphate ions were slightly reduced suggesting this as a mechanism. The effectiveness of calcium and magnesium removal from the wastewater at high pH suggests this is a good approach to the problem. The main challenge for space flight is to find ways of shifting the pH of the wastewater stream that would not require lifting additional, non-reusable/recyclable materials from Earth. Nonetheless, precipitation of struvite and calcium phosphates offers good ways to remove ammonia, magnesium, calcium, and phosphate from the wastewater streams. The precipitates are useful as nutrients for plant growth facilities.

C. Working with an External Partner

Building a pressure vessel safety certified test stand at KSC would have resulted in substantial schedule delays. This led the team to work with the Cerahelix Inc. to validate the filters on their test stand. This complicated certain aspects of the project, such as sample handling and shipping logistics, while simultaneously eliminating the construction of the test stand and advancing the project by six months.

Cerahelix Inc. did not have the ability to do IC analysis or monitor ion flow across their membranes. The research team at KSC was able to provide this ability, while they were able to conduct the filtrations. In the end, a combination of the strengths of both the Cerahelix Inc. and the NASA organizations delivered results within the project time frame. This was a valuable approach and should be considered for future projects where possible.

The results of this project are a success as this was a “high risk, high reward” project with the understanding that there was a high probability of the technology being unable to meet the need. The real goal of these types of projects are twofold: a quick “Go/No go” decision, and “fast failure” meaning get to the answer quickly without investing a great deal of organizational assets to reach the answer. Larger investments can be saved for technologies with higher technology readiness level (TRL) scores.

This project was successful in determining that PicoHelix^{TM} membranes will not meet the rigorous needs for wastewater processing because they are not highly selective in their abilities to remove polyvalent cations from a simulated ISS wastewater stream. Furthermore, the team was able to achieve the goal within the allotted time frame and budget by combining the strengths of NASA and Cerahelix Inc.. The data from the alkaline pH runs conducted for this project strengthen the approach of removing calcium, magnesium, ammonia, and phosphate from the waste streams by precipitation.

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