Advanced Water Purification System for *In Situ* Resource Utilization

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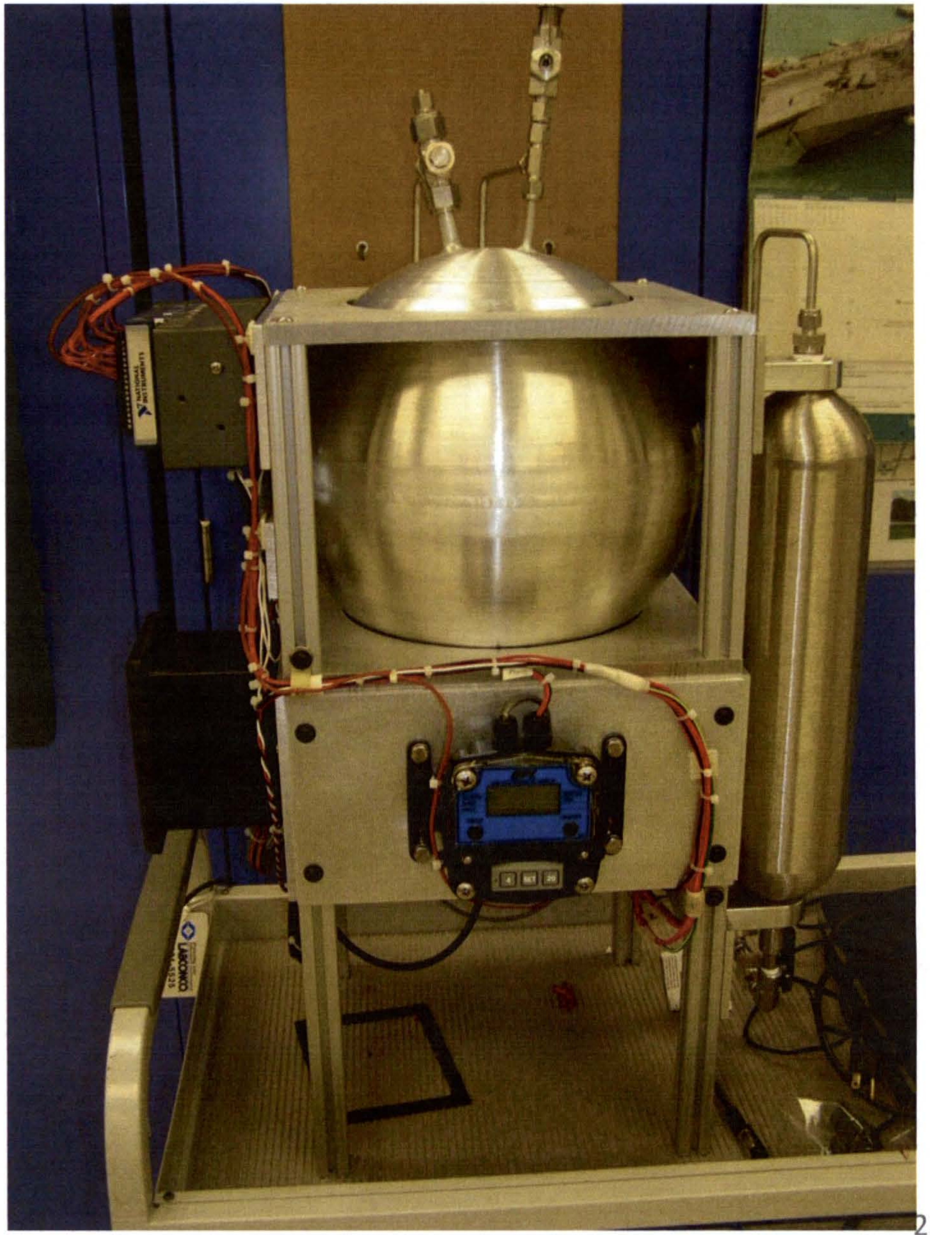
- One of NASA's goals is to enable long-term human presence in space, without the need for continuous replenishment of consumables from Earth.
- *In situ* resource utilization (ISRU) is the use of extraterrestrial resources to support activities such as human life-support, material fabrication and repair, and radiation shielding.
- Potential sources of ISRU resources include lunar and Martian regolith, and Martian atmosphere.



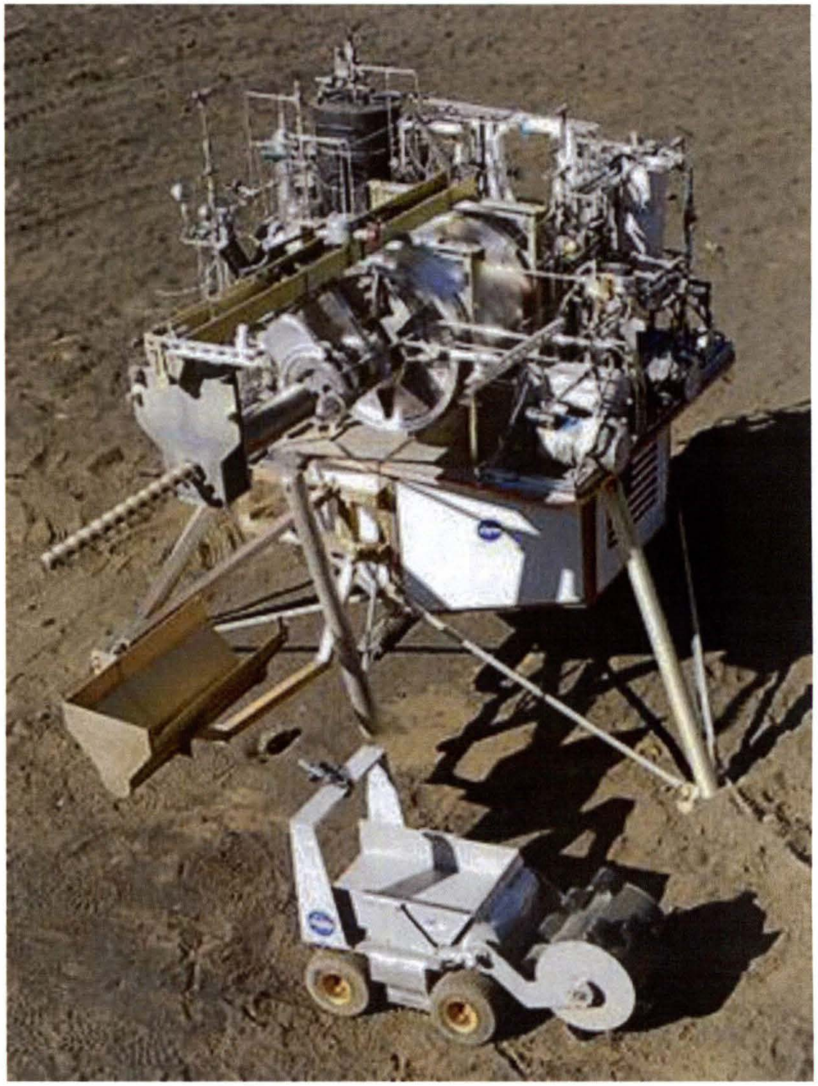
CROPS Mars ISRU Demonstration Unit

Water and Oxygen Production from Lunar Regolith

- Water and byproducts (including hydrochloric and hydrofluoric acids) can be produced from lunar regolith via a high-temperature hydrogen reduction reaction and passing the produced gas through a condenser.

$$FeO + H_2 \xrightarrow{900^\circ C} Fe + H_2O$$

- Due to the high solubility of HCl and HF in water, these byproducts are expected to be present in the product stream (up to 20,000 ppm) and must be removed (less than 10 ppm) prior to water consumption or electrolysis.



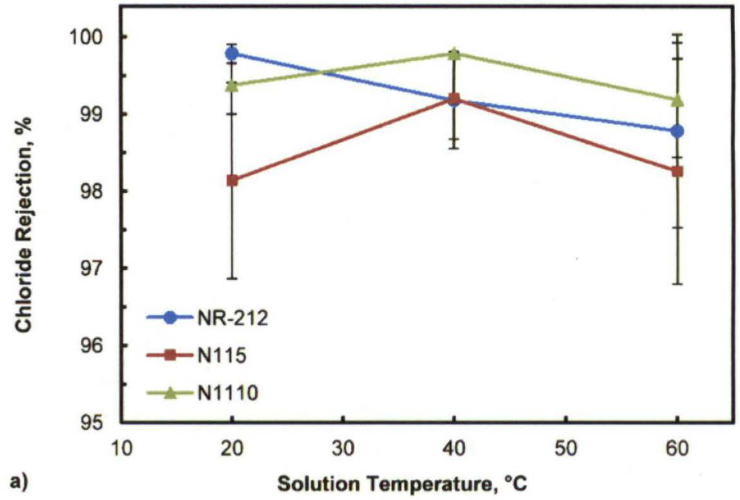
Contaminant Removal Techniques

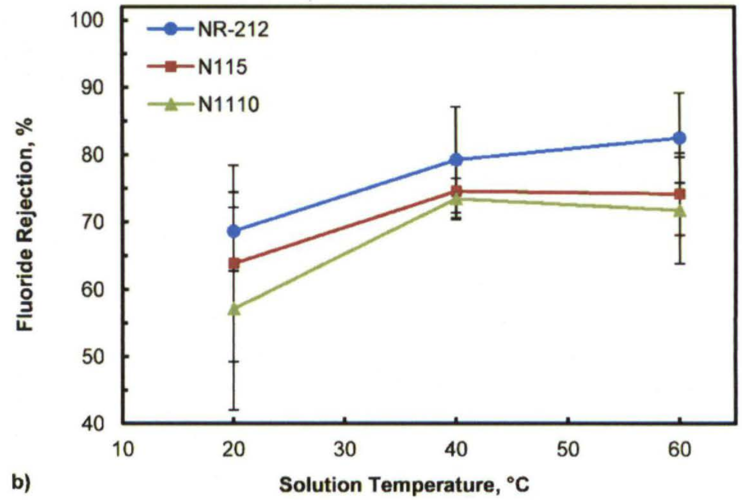
- Due to their consumable nature, typical water purification methods may not be suitable for HCl and HF removal in extraterrestrial applications.
- Membranes and adsorbents are often regenerated with large amounts of water and/or basic solutions, which aren't available in the lunar environment.
- Naturally-occurring adsorbents may be replaced rather than regenerated.

Method	Examples
Membrane (solute retention)	Reverse osmosis
	Nanofiltration
	Proton Exchange
Membrane (solute transport)	Dialysis
	Electrodialysis
	Anion Exchange
Adsorption	Alumina-based adsorbents
	Natural adsorbents (mud, ore, clay, soil, chitosan)

Nafion® Membranes for Contaminant Removal

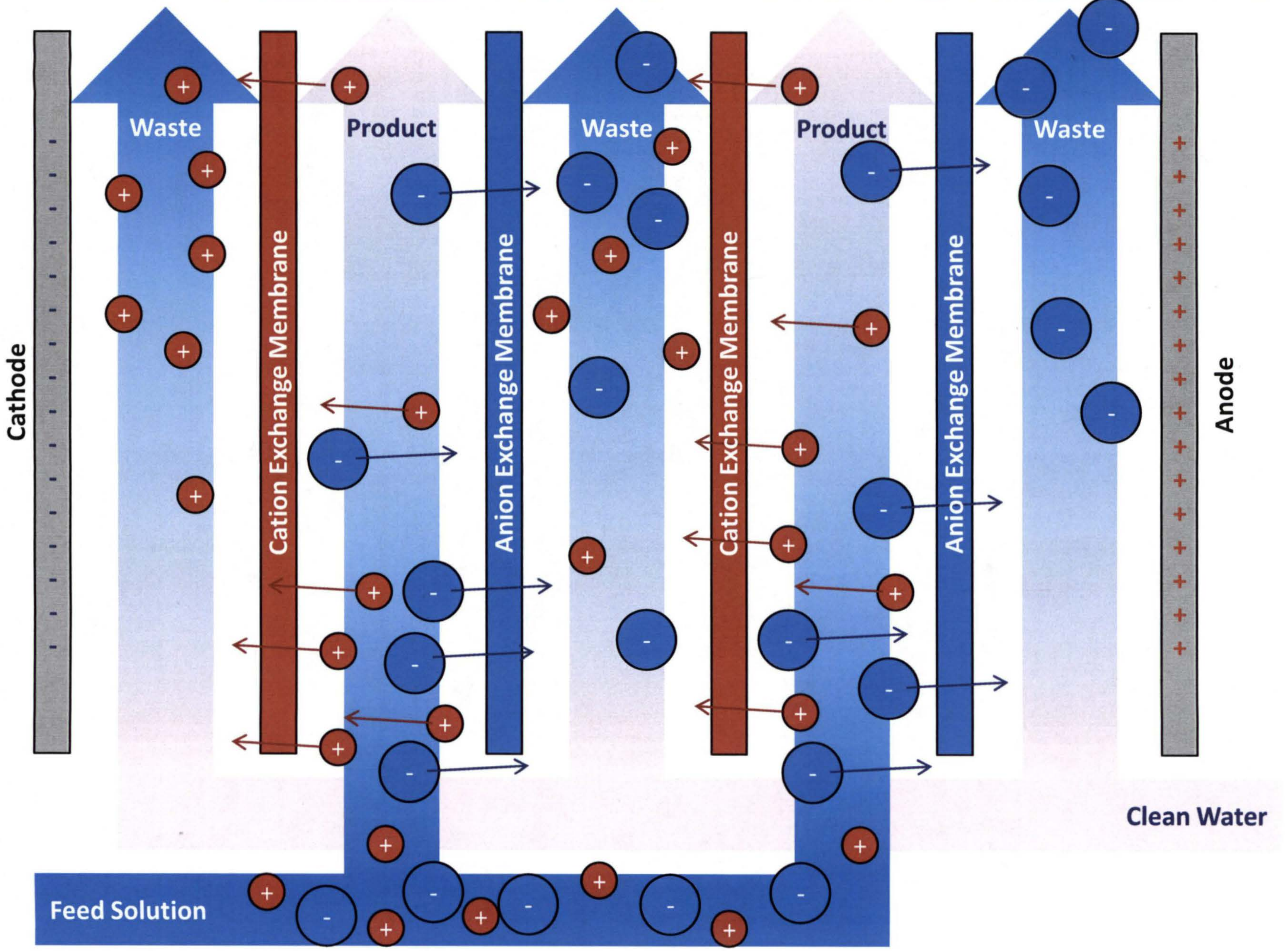
- Nafion®, a common fuel cell proton exchange membrane, was investigated for its chloride and fluoride rejection capability in a previous study
- The ability to reject 98-99.9% of chloride and 50-80% of fluoride was demonstrated
- This rate of rejection was not sufficient to produce electrolysis-grade water
- Since water had to diffuse across the membrane and be recovered in the vapor phase, relatively small amounts of water were recovered using large amounts of carrier gas
- Other technologies were researched with an emphasis on maximizing water recovery and contaminant removal:
  - Higher contaminant removal/rejection rate
  - Contaminant removal/water retention instead of contaminant rejection/water transport
  - Liquid phase only process



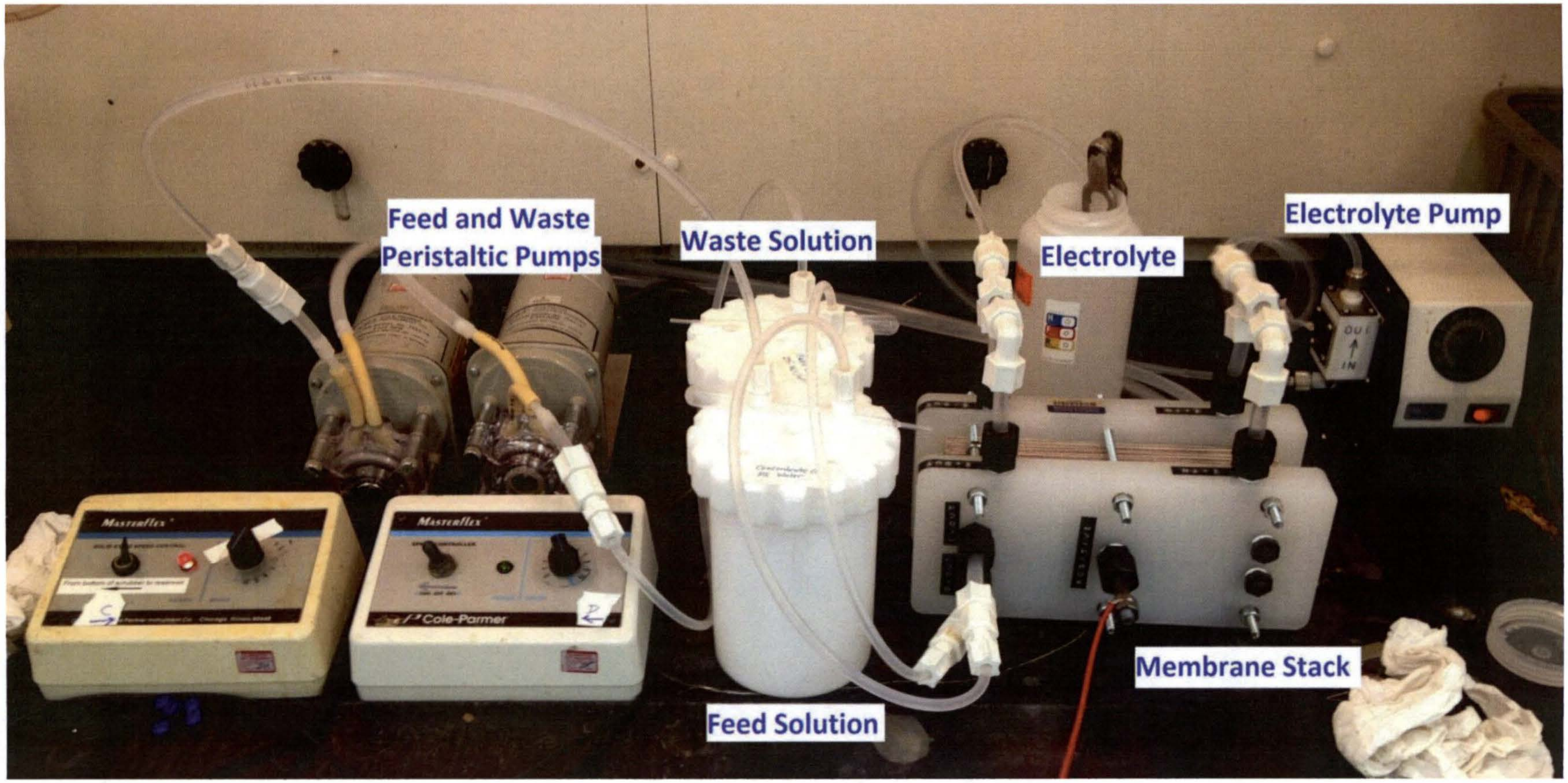


Anthony, S.M., et al. "Contaminant Removal from Oxygen Production Systems for *In Situ* Resource Utilization." *AIAA SPACE 2012 Conference & Exposition*, AIAA 2012-5167.

Electrodialysis for Contaminant Removal



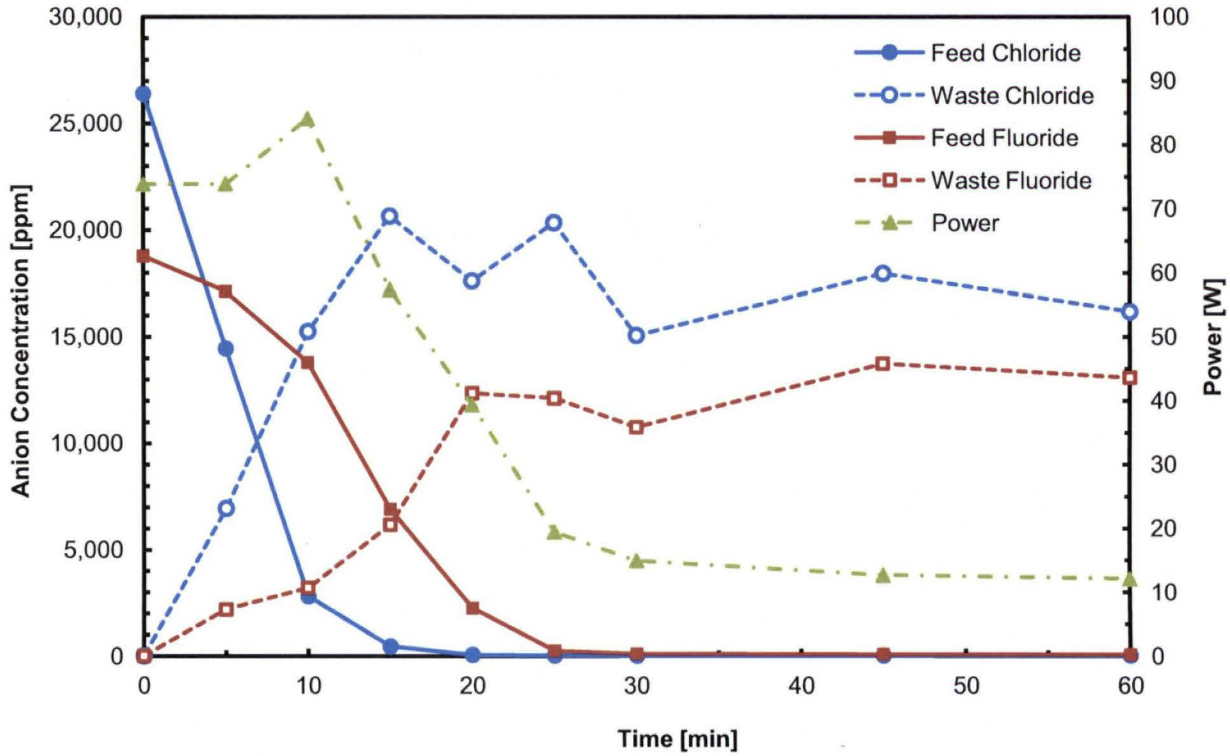
Experimental Apparatus



- High Efficiency Electrodialysis (HEED®) membrane stack purchased from EET Corp.
- Stack contains 20 alternating Ralex® anion and cation exchange membranes
- 0.5% $NaSO_4$ solution circulated through outer cells to protect electrodes

Baseline Contaminant Removal: 20,000 ppm HCl/HF Solution

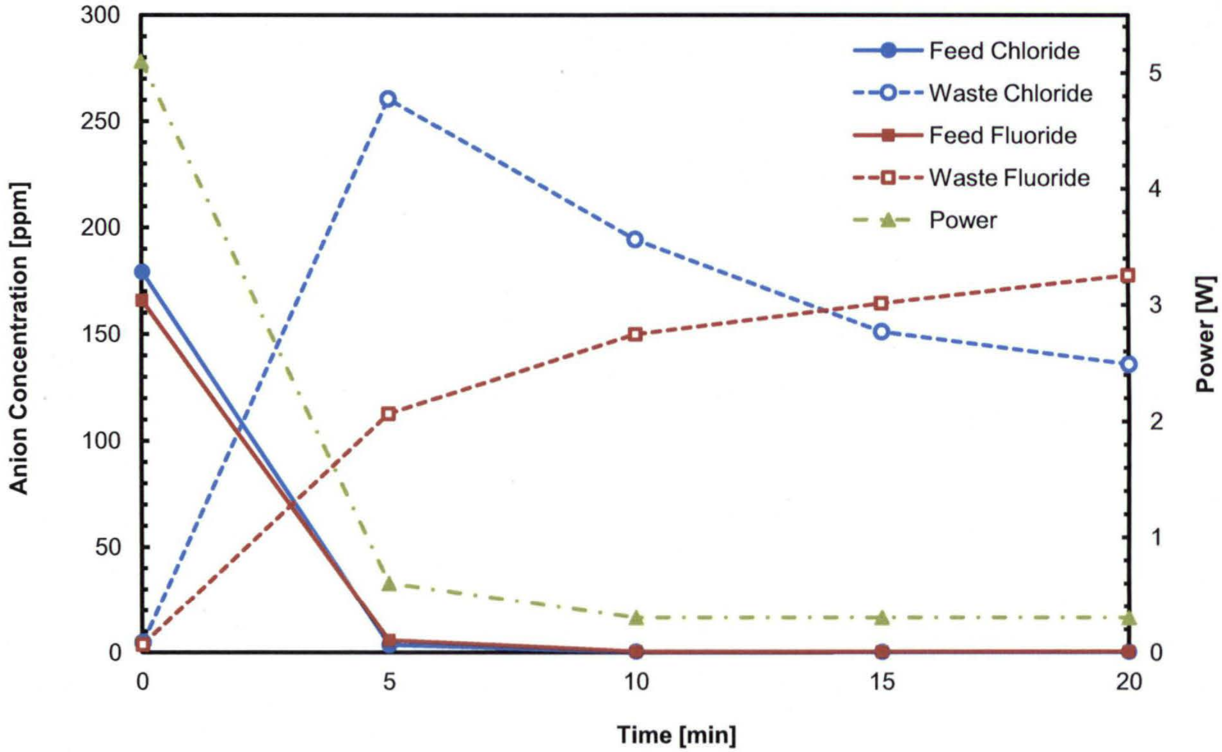
- Starting volume
  - 500 mL diluent
  - 500 mL concentrate
- Final volume
  - 295 mL diluent
  - 685 mL concentrate
- Power supply
  - 30 V maximum
  - 3 A maximum
- Pump speed
  - 100% diluent
  - 100% concentrate
- Reached steady state within 30 min



Diluent Stream	Fluoride	Chloride
Initial (ppm)	18,800	26,400
Final (ppm)	71.1	11.4
Removal (%)	99.44	99.94

Baseline Contaminant Removal: 200 ppm HCl/HF Solution

- Starting volume
  - 500 mL diluent
  - 500 mL concentrate
- Final volume
  - 500 mL diluent
  - 500 mL concentrate
- Power supply
  - 30 V maximum
  - 3 A maximum
- Pump speed
  - 100% diluent
  - 100% concentrate
- Reached steady state in less than 10 min



Diluent Stream	Fluoride	Chloride
Initial (ppm)	166	179
Final (ppm)	0.26	0.07
Removal (%)	99.85	99.96

Variable Matrix Testing: Concentrate Volume

Initial Concentrate Volume (mL)	Final Diluent Volume (mL)	Final Concentrate Volume (mL)	Final Fluoride Concentration (ppm)	Final Chloride Concentration (ppm)
0	170	290	550	23
130	305	310	290	25
250	335	400	167	22
500	295	685	71	11

- Parameters:
  - Initial diluent volume: 500 mL
  - Initial diluent concentration: 20,000 ppm HCl/HF
  - Pump speed: 100% of maximum
  - Voltage: 30 V maximum
  - Current: 3 A maximum
- 130 mL is minimum volume required to fill the concentrate membrane cells and tubing
- Final fluoride concentration decreases substantially with decreasing initial concentrate volume
- Final chloride concentration does not decrease with increasing initial concentrate volume below 250 mL

Variable Matrix Testing: Pump Speed

Pump Speed (% of maximum)	Final Diluent Volume (mL)	Final Concentrate Volume (mL)	Final Fluoride Concentration (ppm)	Final Chloride Concentration (ppm)
< 10	500	510	14,500	13,700
20	280	650	71	8.6
50	300	700	158	20
100	295	685	71	11

- Parameters:
  - Initial diluent volume: 500 mL
  - Initial diluent concentration: 20,000 ppm HCl/HF
  - Initial concentrate volume: 500 mL
  - Voltage: 30 V maximum
  - Current: 3 A maximum
- Pump speed does not affect final fluoride and chloride concentrations, or final diluent and concentrate volumes at or above 20% of maximum setting (at least 200 mL/min)
- Minimum pump speed does not appear to allow for any ion exchange

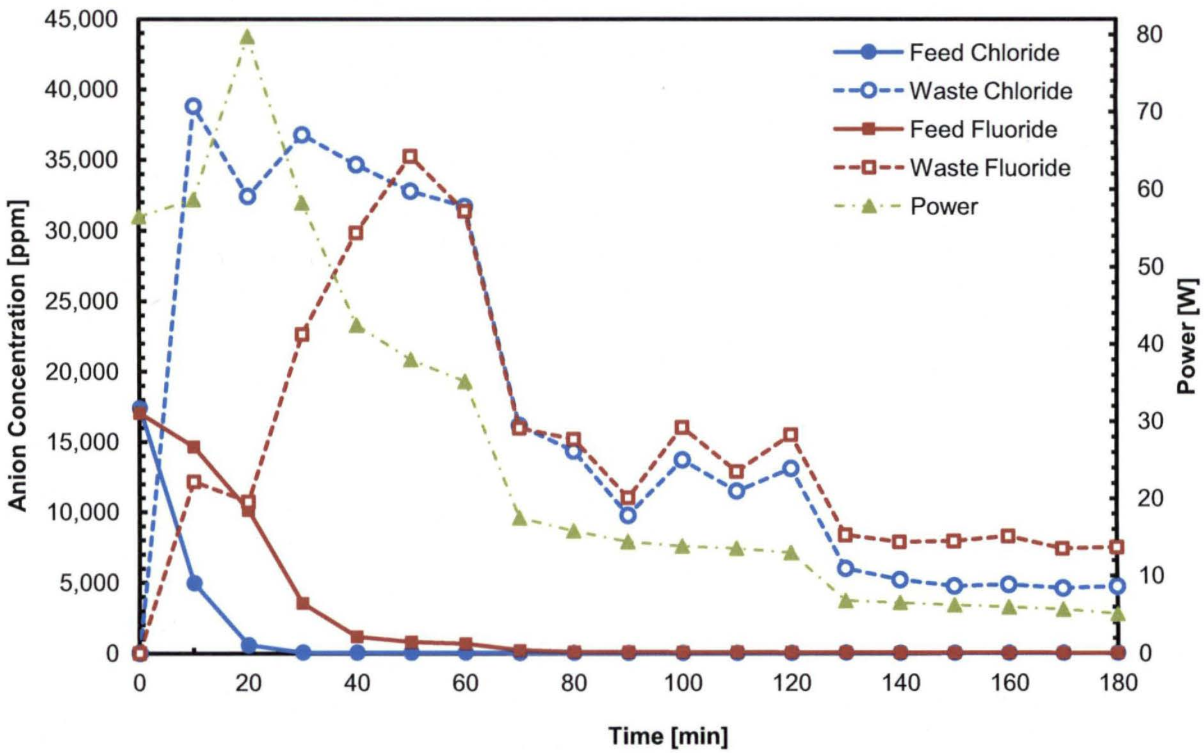
Variable Matrix Testing: Power Supply

<table>
<tr><th>Maximum Voltage (V)</th><th>Maximum Current (A)</th><th>Final Diluent Volume (mL)</th><th>Final Concentrate Volume (mL)</th><th>Final Fluoride Concentration (ppm)</th><th>Final Chloride Concentration (ppm)</th></tr>
<tr><td>30</td><td>3.0</td><td>296</td><td>685</td><td>71</td><td>11</td></tr>
<tr><td>15</td><td rowspan="2">3.0</td><td>325</td><td>675</td><td>1,170</td><td>47</td></tr>
<tr><td>60</td><td>350</td><td>640</td><td>26</td><td>2.8</td></tr>
<tr><td rowspan="2">30</td><td>1.5</td><td>355</td><td>610</td><td>132</td><td>26</td></tr>
<tr><td>6.0</td><td>365</td><td>685</td><td>79</td><td>9.8</td></tr>
</table>

- Parameters:
  - Initial diluent volume: 500 mL
  - Initial diluent concentration: 20,000 ppm HCl/HF
  - Initial concentrate volume: 500 mL
  - Pump speed: 100% of maximum
- Decreasing voltage or current increases final diluent fluoride and chloride concentrations
- Increasing voltage decreases final diluent chloride and fluoride concentrations
- Increasing current does not affect final diluent chloride and fluoride concentrations

ISRU Scenario Testing: Concentrate Replenishment

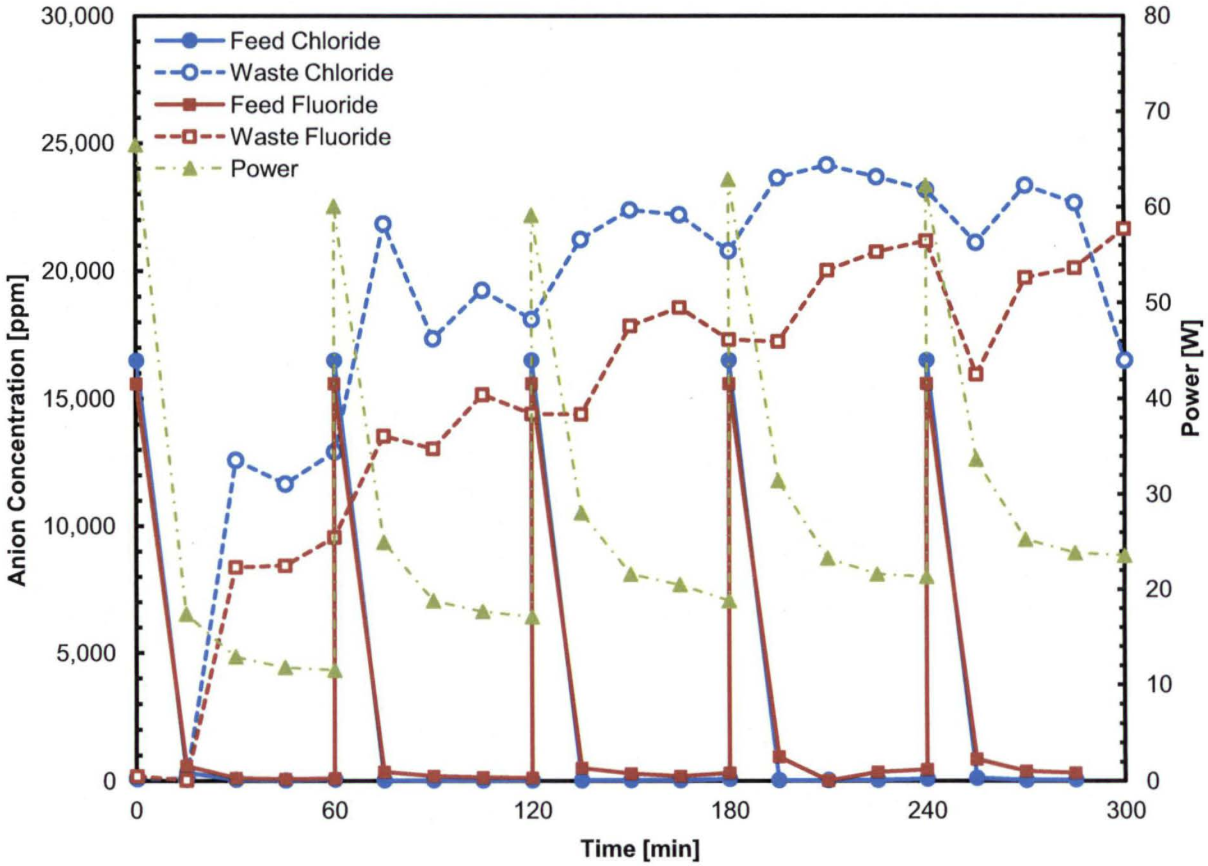
- Initial volumes:
  - 500 mL diluent
  - 100 mL concentrate (replaced every hour, 300 mL total)
- Power supply:
  - 30 V maximum
  - 3.0 A maximum
- Pump speed: 100%
- Final volumes:
  - 250 mL diluent
  - 600 mL concentrate
- Contaminant removal improved versus baseline, but at the expense of longer processing time



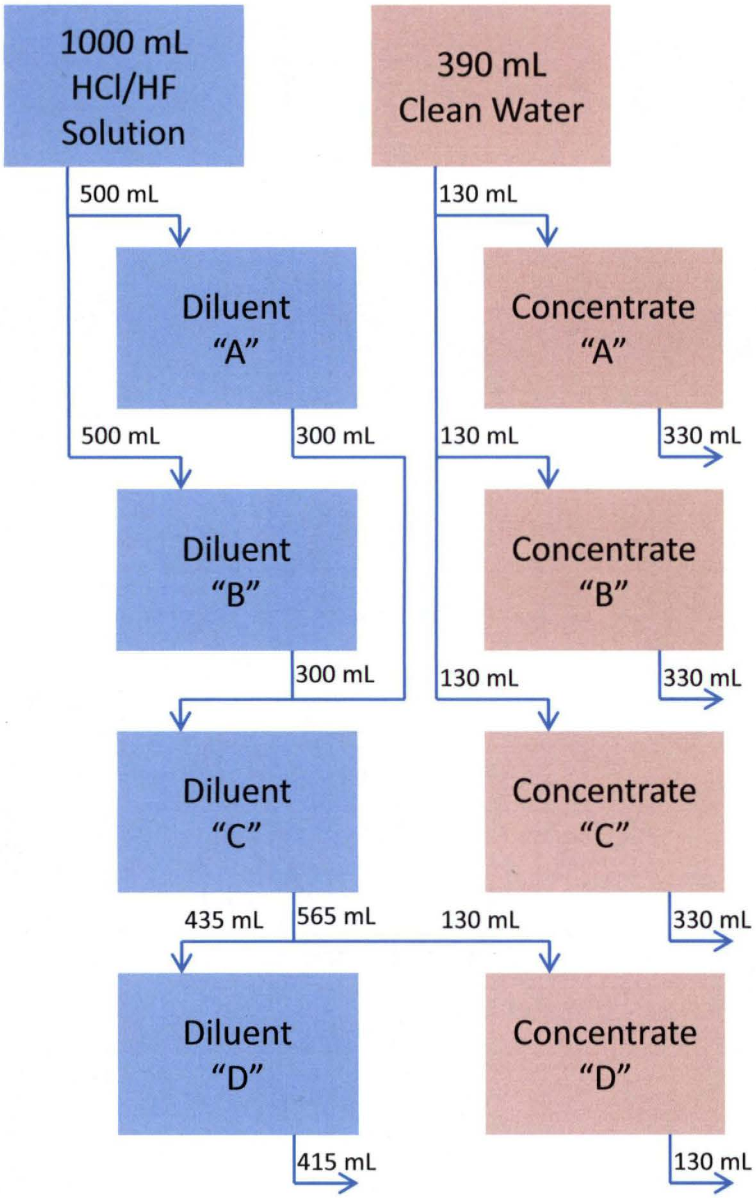
Diluent Stream	Fluoride	Chloride
Initial (ppm)	17,000	17,400
Final (ppm)	27	3.9
Removal (%)	99.92	99.99

ISRU Scenario Testing: Diluent Replenishment

- Initial volumes:
  - 250 mL diluent (replaced every hour, 1250 mL total)
  - 250 mL concentrate
- Power supply:
  - 30 V maximum
  - 3.0 A maximum
- Pump speed: 100%
- Final volumes:
  - 360 mL diluent
  - 830 mL concentrate
- Contaminant removal was not significantly improved versus simply processing at a higher diluent to concentrate volume ratio



ISRU Scenario Testing: Obtaining Electrolysis-Grade Water



Diluent "A"	Fluoride	Chloride
Initial (ppm)	14,200	15,100
Final (ppm)	736	124
Removal (%)	94.8	99.2

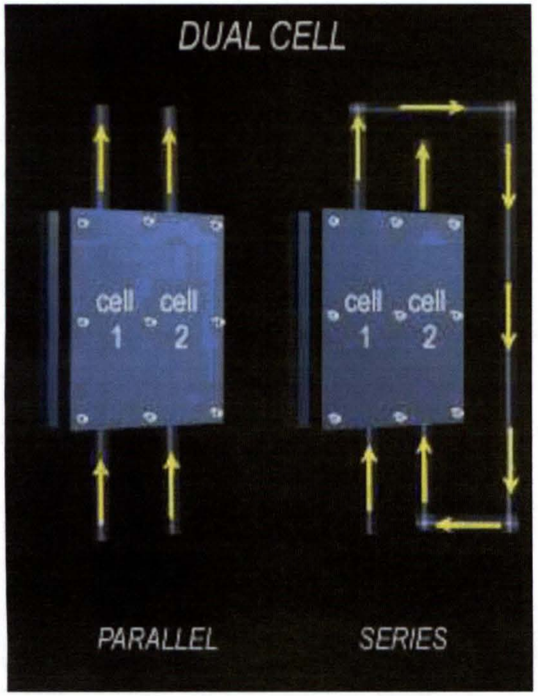
Diluent "B"	Fluoride	Chloride
Initial (ppm)	16,200	19,000
Final (ppm)	214	126
Removal (%)	98.7	99.3

Diluent "C"	Fluoride	Chloride
Initial (ppm)	1,140	222
Final (ppm)	12.6	10.9
Removal (%)	98.9	95.1

Diluent "D"	Fluoride	Chloride
Initial (ppm)	80.4	41.4
Final (ppm)	0.41	0.16
Removal (%)	99.5	99.6

Future Work: System Optimization

- Added new and additional components to increase system robustness and minimize processing time:
  - Larger membrane stack that contains two 20 membrane cells which can run in series or parallel
  - Higher voltage/current power supply to achieve rapid equilibrium
  - In-line conductivity meters for real-time measurement of water purity
  - Hastelloy® electrodes which offer superior protection against hydrofluoric acid versus stainless steel



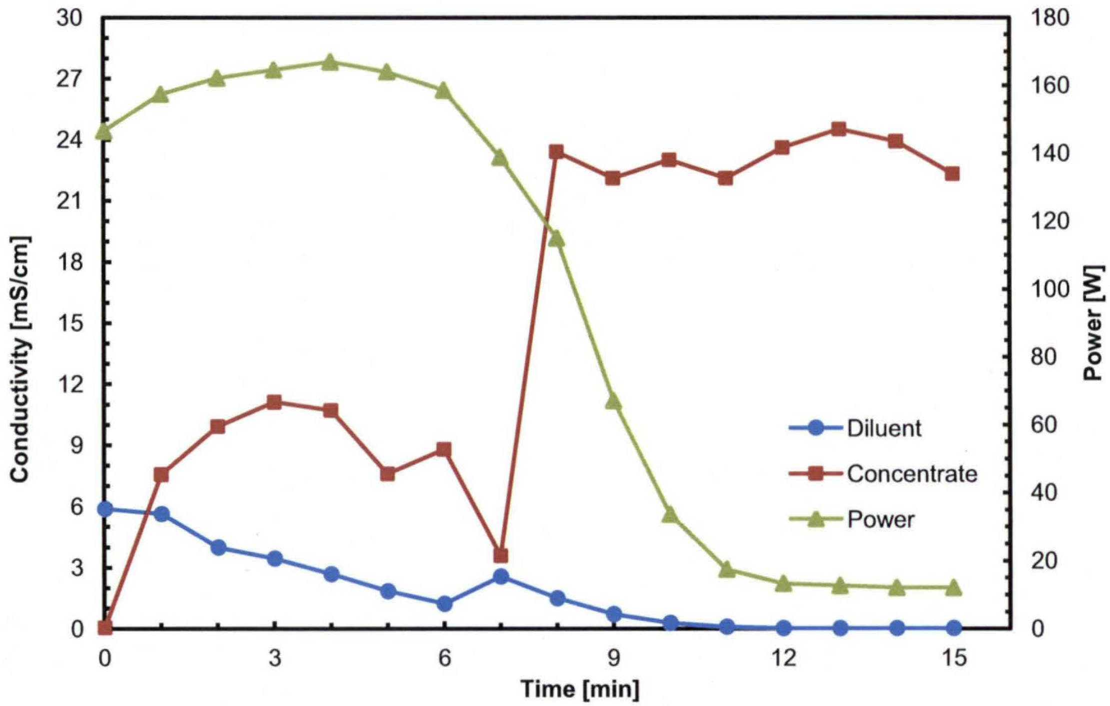
http://www.eetcorp.com/lts/flowconfig.htm

- Other considerations for future work:
  - Different types of anion/cation exchange membranes
  - Alternate membrane stack configurations
  - Integration with additional water processing unit (e.g., Nafion®)
  - Increase system automation

Future Work: Mars ISRU Water Purification

Ion	C (wt%)	C_{th} (wt%)
Na^+	0.27	0.10
Mg^{2+}	0.44	0.60
K^+	0.28	0.03
Ca^{2+}	0.05	0.04
Cl^-	0.79	0.04
ClO_4^-	0.72	0.60
HCO_3^-	0.73	?
SO_4^{2-}	0.78	?

Kounaves, S.P., et al. "Aqueous Carbonate Chemistry of the Martian Soil at the Phoenix Landing Site," *40th Lunar and Planetary Sciences Conference*, 2009.



- Attemped to simulate ionic contaminants in water recovered by Phoenix lander
- In absence of specific ion standards, measured contaminant removal indirectly via conductivity meters in diluent and concentrate streams
- Achieved minimum diluent conductivity after about 10 min

Acknowledgements

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