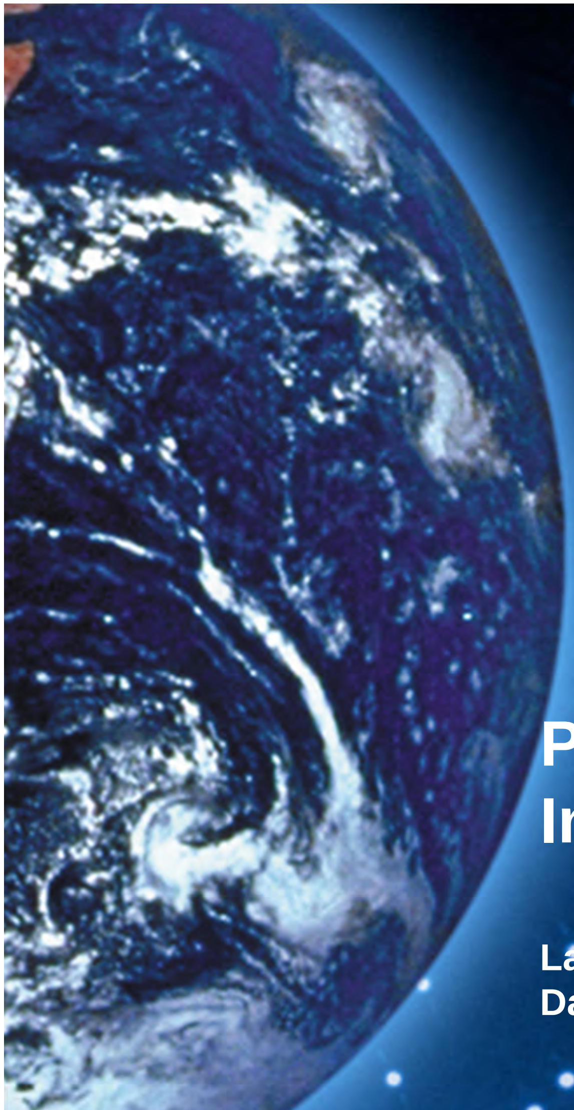

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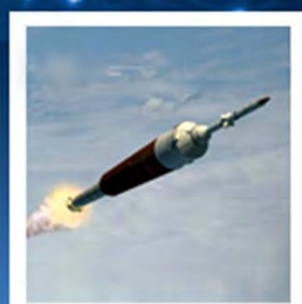
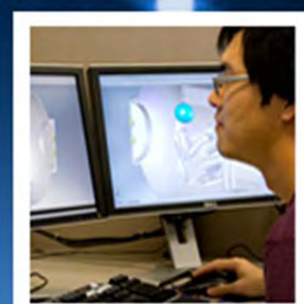
Life has no limits.

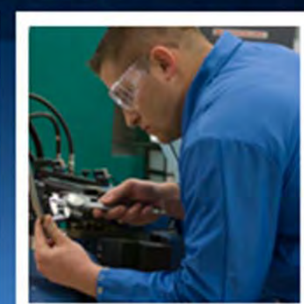
Purifying Water Mined from Asteroids for In Situ Resource Utilization

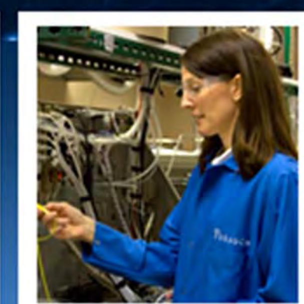
Laura Kelsey, Paragon SDC

Dante Lauretta, PhD, OSIRIS-Rex Principal Investigator, University of Arizona







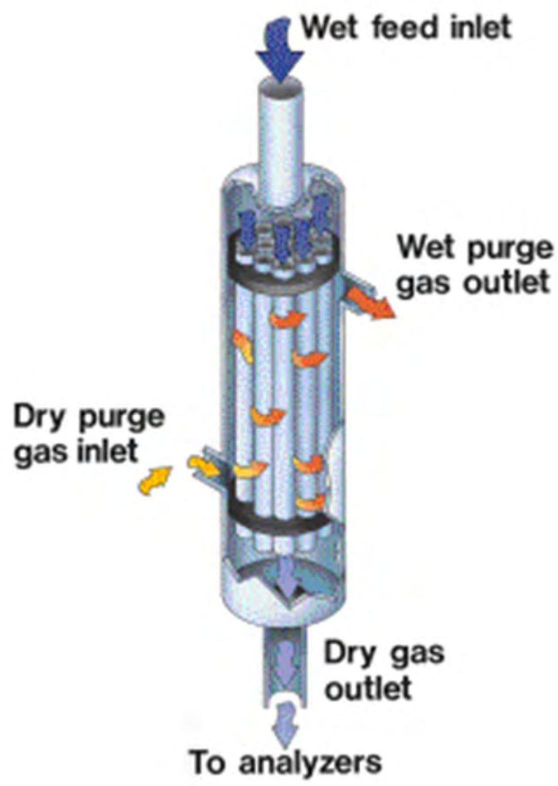


Contaminant Robust In Situ Water Extractor

- CRIWE
  - Nafion-based water clean-up
  - Extract purified water from natural extraterrestrial sources
  - *In situ* water processing for downstream electrolysis
  - Chemically resistant to process contaminants such as acid

Background on Nafion

- Cation exchange ionomer with Teflon backbone
- Extremely chemically resistant
- Selectively permeable
- Water bonds to sulfonic acid groups as water of hydration to permeate through membrane
- Permeation driven by water vapor partial pressure differential
  - Partial pressure differential can be achieved by purge gas or vacuum



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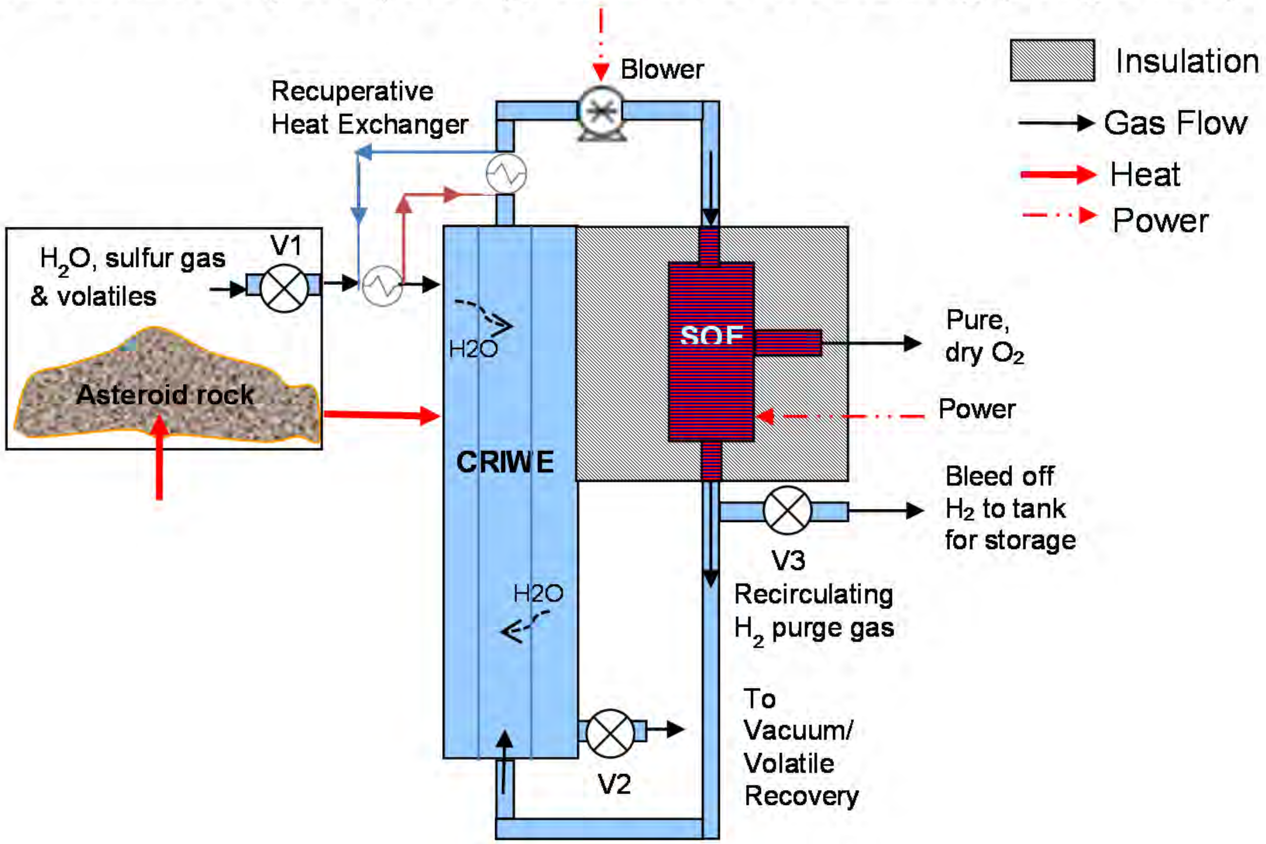
Operational Concept 1

- Water extraction system from asteroids using CRIWE, Solid Oxide Electrolysis (SOE), and a recirculating purge loop



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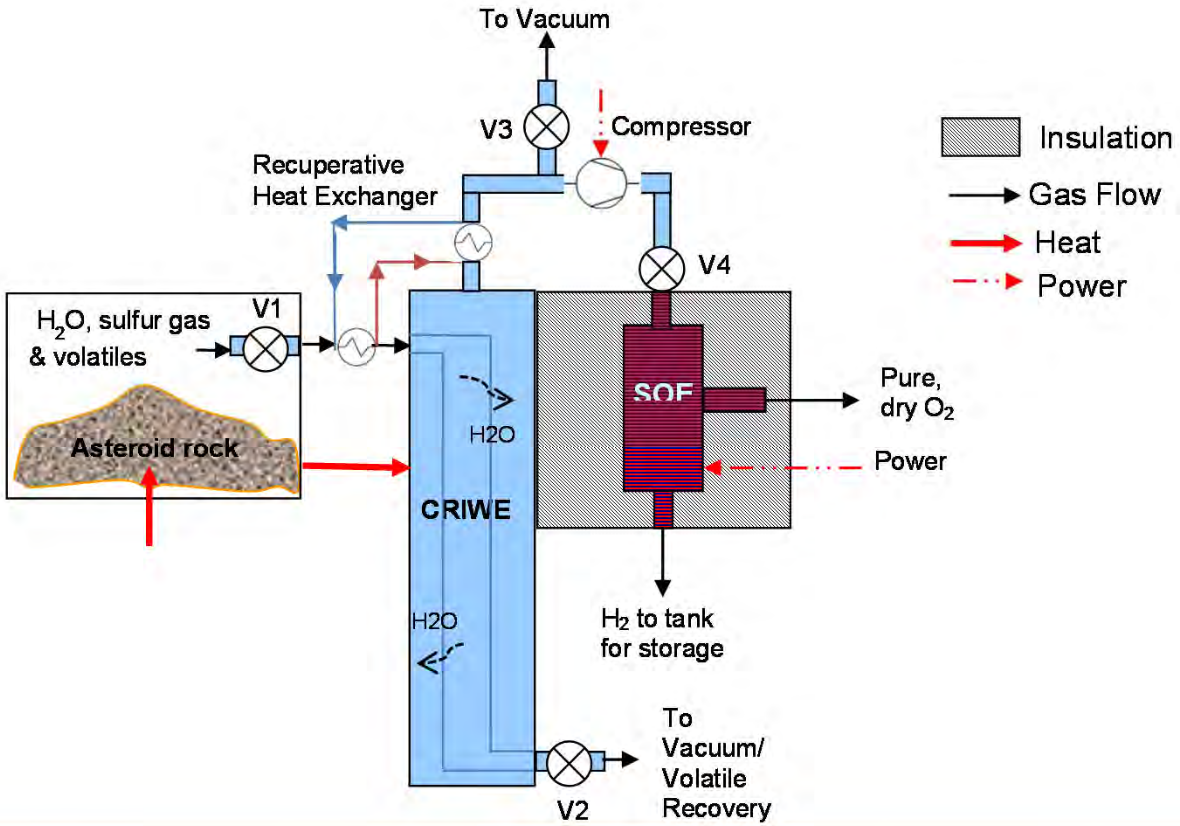
Operational Concept 2

- Water extraction system from asteroids using CRIWE, SOE, and no carrier gas (vacuum drives permeation)



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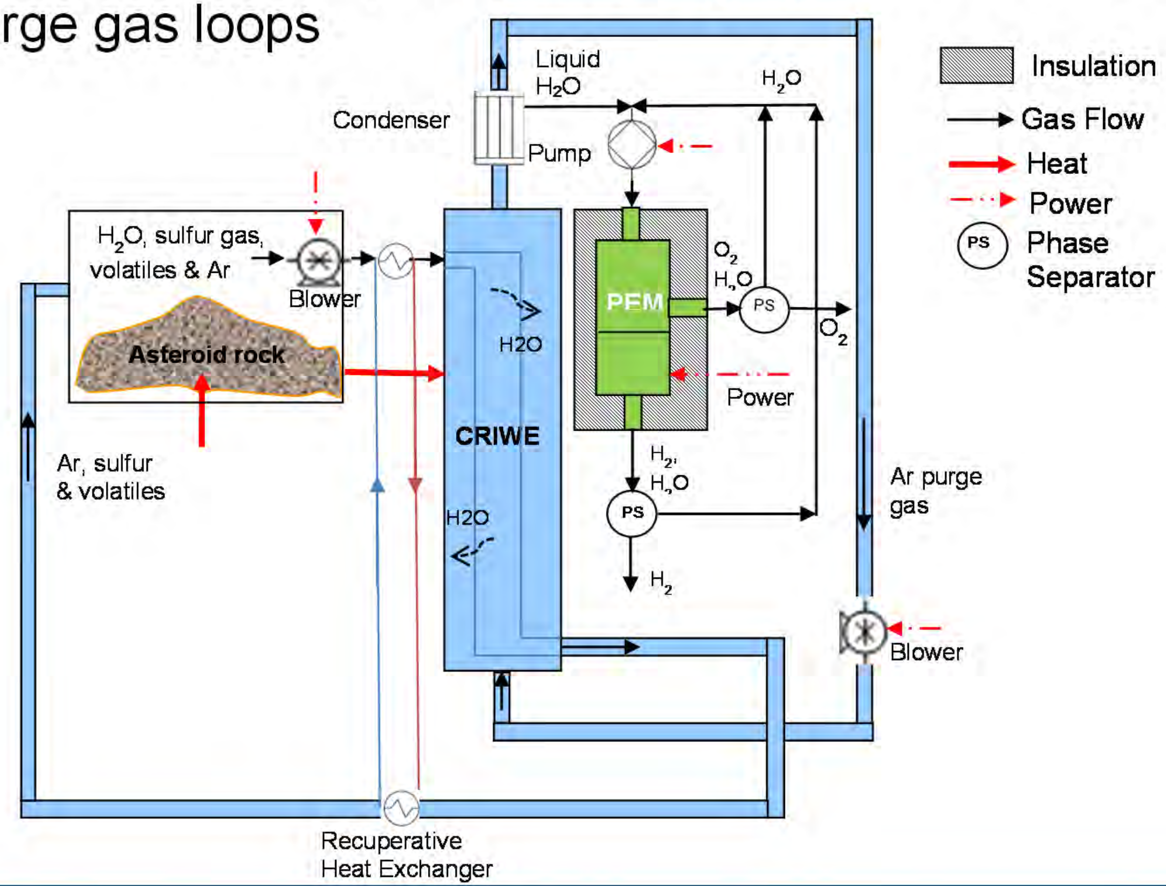
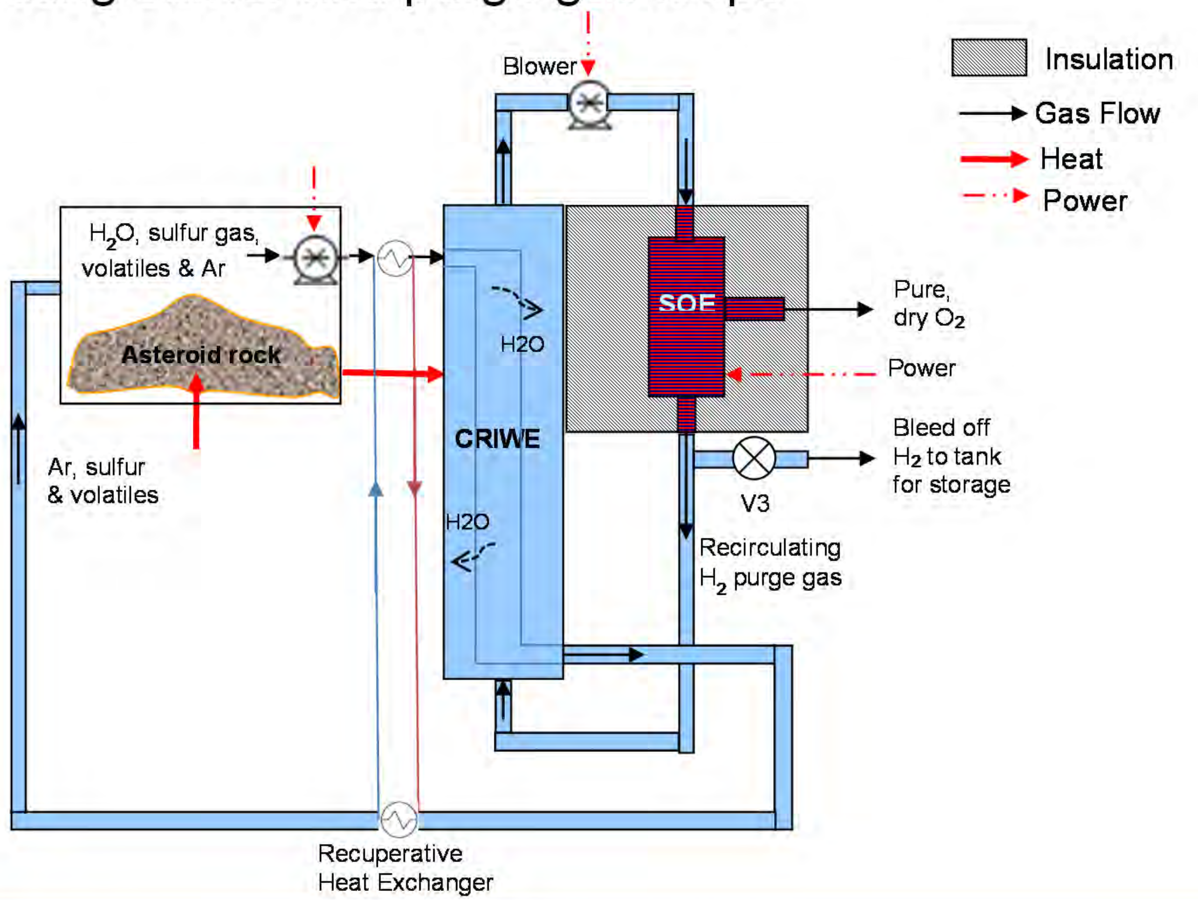
Operational Concept 3

- Water extraction system from asteroids using CRIWE, Proton Exchange Membrane (PEM) Electrolysis, and recirculating carrier and purge gas loops



Operational Concept 4

- Water extraction system from asteroids using CRIWE, SOE and recirculating carrier and purge gas loops

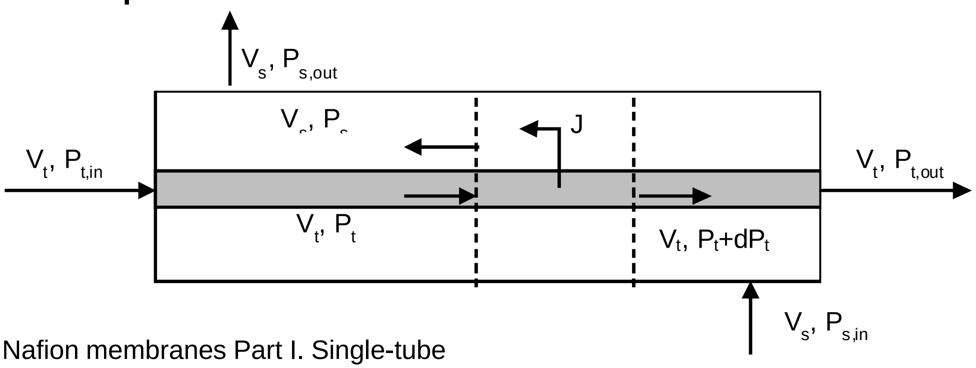


System Analysis of Operational Concept 4

- Chemical and thermodynamic analysis:
  - Soil Chamber chemistry
  - Blower
  - Heat exchanger
  - CRIWE moisture exchange
  - Electrolysis

Water Transport through Nafion

- Water binds to exposed sulfonic acid group on surface
- Permeates through the membrane by rapidly transferring from sulfonic acid to adjoining sulfonic acid within the ionic channels
- Pervaporates from a bound solid state directly into the vapor phase in the surrounding gas at outside surface
- Highly water-soluble gases may bind to the water molecule while it is still exposed on the Nafion surface and permeate through membrane with water molecule
- Permeation driven by water vapor partial pressure differential
- Permeation model based on work by Ye and LeVan[1]
- Mass transfer coefficients derived from heat transfer correlations and empirical data



[1]Ye, Xinhuai and M. Douglas LeVan, "Water transport properties of Nafion membranes Part I. Single-tube membrane module for air drying," *Journal of Membrane Science* 221 (2003) 147. Print.

Asteroid Selection

- Meteorite Classes and Compositions
- Assume all H is in the form H_2O

Prevalence	Class	Name	C (%)	H (%)	N (%)	S (%)
9 known A1	CH	Orgueil	3.31	2.22	0.19	4.94
416 known	CM2	Murchison	1.99	1.38	0.09	2.97
134 known	CR2	EET 92042	1.09	0.43	0.07	1.18
336 known	C03	Kainsaz	0.64	0.13	0.13	1.69
256 known	CV3	RBT 04133	0.59	0.37	0.02	1.90
		Allende	0.33	0.03	0.02	1.95
117 known	Martian	NWA 4783	0.06	0.02	0.00	0.06

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Slide 10

A1 These could use better descriptions. Dante?
Author, 28/04/2013

Murchison Mineralogy

- Murchison consists of
  - Olivine $(MgFe)_2SiO_4$ – 15%
  - Pyroxene $XY(SiAl)_2O_6$ – 8.3%
  - Calcite $CaCO_3$ – 1.2%
  - Magnetite FeO_4 – 1.1%
  - Fe-cronstedtite $Fe_2^{2+}Fe^{3+}(SiFe^{3+}O_5)(OH)_4$ – 50%
  - Mg-serpentine $(MgFe)_3Si_2O_5(OH)_4$ – 22%
  - Pentlandite $(FeNi)_9S_8$ – 0.65%
  - Pyrrhotite $Fe_{1-x}S$ – 1.2%[1]
  - Tochilinite $6Fe_{.9}S{\cdot}5(MgFe{+}{+})(OH)_2$ – <1%[2]
  - Troilite FeS
- Cronstedtite, Mg-serpentine, and tochilinite contain water
- Murchison meteorite is 12% water by mass[3]

[1]Howard, K.T. et al. *Modal mineralogy of CM2 chondrites by X-ray diffraction (PSD-XRD). Part 1: Total phyllosilicate abundance and the degree of aqueous alteration,* Geochimica et Cosmochimica Acta, 73, 2009, 4576-4589.
[2]Zolensky, M.E. et al. *Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites.* Geochimica et Cosmochimica Acta 57, 1993, 3123-3148
[3] Fuchs, Louis, et al. *Mineralogy, Mineral-Chemistry, and Composition of the Murchison (C2) Meteorite.* Smithsonian Contributions to the Earth Sciences. Number 10, Smithsonian Institution Press. City of Washington. 1973.

Water Release

- Heating to 700°C at near atmospheric pressure (101 kPa) required to reach activation energy for release of H_2O
- High-precision kinetic experiment measured elemental counts of vapors released during heating of meteorite sample to 700°C
- Experiment did not measure water – concentration of each element with respect to water was calculated based on measured release during experiment and using $12\%_m$ meteorite water content

Vapor Composition

- Trace element content of water released from the Murchison Carbonaceous Meteorite at 700°C
- Note extremely high concentration of sulfur, as well as mercury and lead
- Sulfur poisons platinum electrodes in electrolyzers, leading to irreversible losses in platinum electrode performance.
- The deactivation of Pt sites is independent of the type of sulfur contamination[1]
- Nafion theoretically impermeable to sulfur compounds resulting from analysis

[1]Sethuraman, Vijay and John W. Weidner. "Analysis of sulfur poisoning on a PEM fuel cell electrode" *Electrochimica Acta* 55, 2010, 5683-5694.

Trace element	Concentration with respect to water release	Units
S	50000	mg/L
Zn	15	mg/L
As	0.41	mg/L
Se	0.95	mg/L
Cd	2.7	mg/L
In	3.7	mg/L
Sn	2.8	mg/L
Sb	0.02	mg/L
Te	0.11	mg/L
Au	0.83	mg/L
Hg	7.9	mg/L
Tl	0.51	mg/L
Pb	27	mg/L
Bi	0.31	mg/L

Sulfur Release

- Sulfur bearing compounds: Pentlandite, Pyrrhotite, Tochilinite & Troilite
- Pentlandite breaks down into $Ni_{3\pm x}S_2$ and pyrrhotite at 610°C or above (though a high form can exist up to 865°C before breaking down into pyrrhotite)[1]
- At 327-397°C, troilite transforms into pyrrhotite
- At temperature higher than 397°C, pyrrhotite dissociates into Fe and S[2]
- Sulfur vaporizes and exists as S_2 through S_8, depending on temperature

$$FeS \xrightarrow{T<397°C} Fe_{1-x}S + xFe$$

$$(1-x_2)Fe_{1-x}S \xrightarrow{T>397°C} (1-x)Fe_{1-x_2}S + (x-x_2)S$$

[1]Sugaki and Kitakaze, *High form of pentlandite and its thermal stability*, American Mineralogist, Vol. 83, 1998, 133-140.
[2]Selivanov et al., *Theramal Expansion of Troilite and Pyrrhotine in Helium and Air,* Inorganic Materials, Vol. 39, No. 10, 2003, 1097-1102.

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Volatiles Chemistry in CRIWE system

- Oxygen production rates of 1, 10, and 100 kg O_2/day assumed to demonstrate scaling
- 700°C, 140 kPa in reactor
- Utilize Ar as a sweep gas
- Chemical Equilibrium with Applications (CEA) of NASA Glenn Research Center used to perform equilibrium analysis
- Upon exiting the reactor, the stream must be cooled to ~110°C prior to entering CRIWE because Nafion has a maximum operating temperature of 150°C.

CEA Analysis Results

Stage 1 (Reactor)					Stage 2 (pre-CRIWE cool down)			
	Seed	700°C	Equilibrium			Seed	110°C	Equilibrium
Species	Molar fraction	Species	Molar fraction		Species	Molar fraction	Species	Molar fraction
H2O	0.7568	H2O	0.6788		H2O	0.6788	H2O	0.6924
S8	0.0133	H2S	0.05616		H2S	0.05616	H2S	0.00034
Ar	0.2299	Ar	0.2241		Ar	0.2241	Ar	0.2104
		SO2	0.02927		SO2	0.02927	SO2	0.00017
		H2	0.00268		H2	0.00268	S8	0.00001
		S2	0.00859		S2	0.00859	S(b)	0.09668
		S2O	0.0003		S2O	0.0003		
		S3	0.00014		S3	0.00014		

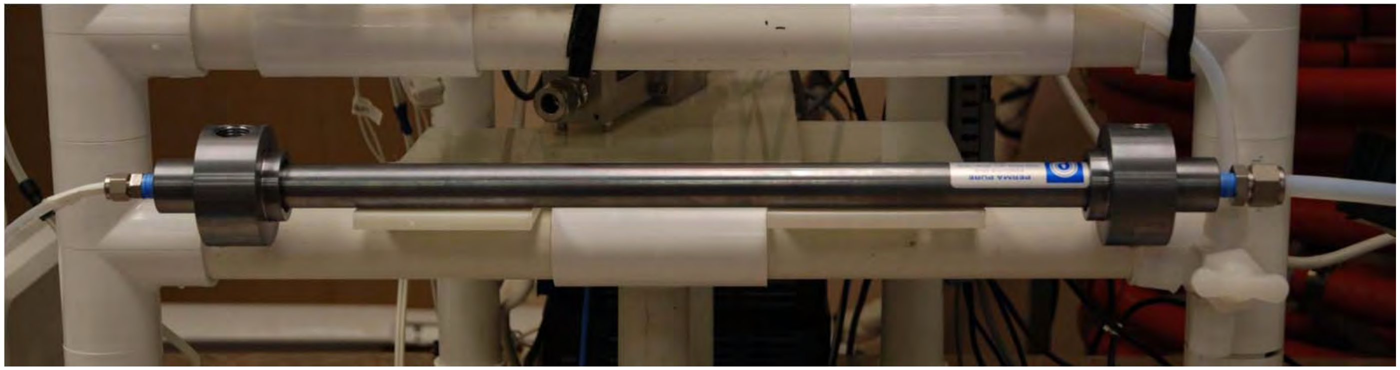
Analysis Results

Parameter	1 kg/day	10 kg/day	100 kg/day
O_2 production rate	1.18 kg/day	9.83 kg/day	94.9 kg/day
H_2O extraction rate	1.17 kg/day	11.7 kg/day	112 kg/day
% H_2O extraction	99%	99%	95%
Raw material processing rate	8.46 kg/day	84.6 kg/day	846 kg/day
Tube Operating Pressure	145 kPa	145 kPa	155 kPa
Tube Operating Temperature	110°C	110°C	110°C
Tube Ar flow rate	0.34 SLPM	3.4 SLPM	34 SLPM
Shell Operating Pressure	105 kPa	105 kPa	105 kPa
Shell Operating Temperature	87°C	87°C	120°C
Shell H_2 flow rate	2 SLPM	20 SLPM	275 SLPM
CRIWE Length	0.2 m	0.3 m	0.6 m
# of Nafion tubes	25	50	200
Nafion tubes ID	0.64 mm	0.64 mm	0.64 mm
Nafion tubes OD	0.84 mm	0.84 mm	0.84 mm
Electrolysis Power	249 W	2478 W	2385 kW
Remaining System Power	81 W	807 W	8.8 kW

Related Experimental Results

- An EDU was built and tested for a water extraction/oxygen production system for Mars
  - Primary contaminants were Cl_2 and HCl
- Average water recovery of 93% achieved
- CRIWE prevented 95% to 99% of contaminants from ending up in extracted product water
- Contaminant reduction increased with increasing purge gas flow rate relative to sample flow rate

EDU Images



Conclusions

1. Water extraction system can theoretically be used for asteroid mining
2. Extraction can be performed with either purge gas or vacuum to drive permeation
3. Nafion is theoretically impermeable to expected contaminants
4. The CRIWE unit is compact, flexible and provides a simple process for water extraction with no extreme temperature or power requirements and works in single-phase fluid flow with no moving parts

Acknowledgments

I would like to thank Taber MacCallum who had the original idea of using Nafion for in situ water extraction and Dante Lauretta for his contributions to the asteroid selection and mineralogy work.