

## Oxygen Production from Lunar Regolith using Ionic Liquids

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The objective of this work and future follow-on work is to develop a safe, efficient, and recyclable method for oxygen and/or metals extraction from lunar regolith, in support of establishing a manned lunar outpost. The approach is to solubilize the oxides that comprise lunar regolith in media consisting of ionic liquids (ILs) and/or their mixtures at temperatures at or below 300°C. Once in solution, electrolysis can either be performed in-situ to generate oxygen at the anode and hydrogen and/or metals (silicon, iron, aluminum, titanium, etc.) at the cathode. Alternatively, the water that is generated during the solubilization process can be distilled out and condensed into a separate IL and then electrolyzed to produce hydrogen and oxygen. In the case of lunar regolith, this method could theoretically produce 44g oxygen per 100g of regolith. The oxygen can be used for human life support and/or as an oxidizer for rocket fuels, and the metals can be used as raw materials for construction and/or device fabrication. Moreover, the hydrogen produced can be used to re-generate the acidic medium, which can then be used to process additional regolith, thereby making the materials recyclable and limiting up-mass requirements. An important advantage of IL acid systems is that they are much "greener" and safer than conventional materials used for regolith processing such as sulfuric or hydrochloric acids. They have very low vapor pressures, which means that they contain virtually no toxic and/or flammable volatile content, they are relatively non-corrosive, and they can exhibit good stability in harsh environments (extreme temperatures, hard vacuum, etc.). Furthermore, regolith processing can be achieved at lower temperatures than other processes such as molten oxide electrolysis or hydrogen reduction, thereby reducing initial power requirements.

Six ILs have been synthesized and tested for their capability to dissolve lunar simulant, and for electrochemical and thermal stability. The results showed that ILs can be very efficient electrolytes; in particular, IL/phosphoric acid mixtures appear extremely promising for solubilizing lunar simulant. Results from preliminary experiments for distillation of water produced from the oxygen within the metal oxides of the simulant and the hydrogen from the acid indicates that **over 75% of the oxygen from the simulant can be harvested as water at a temperature of 150° C.** A method for collection of oxygen from electrolysis of the water derived from solubilizing simulant was developed by using a liquid nitrogen trap to liquefy and collect the oxygen. Although precise quantification of the liquid oxygen trapped is difficult to obtain, **the amount of hydrogen and oxygen collected from electrolysis of water in this system was greater than 98%.** This set-up also included a portable mass spectrometer for the identification of gases released from electrolysis cells. Regeneration of ILs through re-protonation was also demonstrated. **Four sequential regenerations of an IL following solubilization of simulant showed no significant differences in amounts of simulant dissolved.**

Follow-on work for this project should include more studies of IL/phosphoric acid systems. Also, much more work is necessary for defining methods for electrolysis and purification of metals from regolith solubilized in ILs, and for developing a system to use the produced

hydrogen to regenerate the spent IL. Finally, design and development of flight breadboard and prototype hardware is required.



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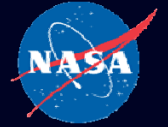
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## Oxygen Extraction from Lunar Regolith - Overview

Achieving NASA's goal of establishing a sustainable manned lunar outpost will require the extraction of oxygen from lunar regolith (soil) in a safe manner that minimizes consumables and energy. Methods include:

- Molten Oxide Electrolysis – Requires High Temperature and Refractory Materials
- Hydrogen Reduction – Low Yield of Oxygen per Unit Mass of Regolith (1%)
- Chemical Beneficiation – Requires Launching, Storing, and Handling of Hazardous, Corrosive, and/or Toxic Reagents



## Ionic Liquids for NASA Applications

Ionic Liquids (ILs) are comprised solely of oppositely charged ions. Because of their novel properties they show great promise as the next generation of chemical reagents. ILs are also ideally suited for meeting some of the challenges of NASA's space exploration goals:

- Green – Low Vapor Pressure and Low Flammability
- Space Durable – Stable in Extreme Temperatures and Hard Vacuum
- Versatile – Molecular Structure can be “engineered” to be Task Specific (Epoxyes, Adhesives, Lubricants, Structural Components, Oxygen Production)



## Methodology and Approach

Because of their design flexibility, ILs can possess all the functionality of conventional materials. Hence they offer a safer alternative to hazardous reagents for the beneficiation of lunar regolith and extraction of oxygen.

### Experimental Approach:

- 1) Solubilization of regolith in IL medium to convert metal oxides to water and metallic ions.
- 2) Electrolysis of water produced to generate oxygen and hydrogen.
- 3) Regeneration of IL medium by electrolysis of hydrogen by-product using hydrogen gas electrode.



## Solubilization of Lunar Regolith in Ionic Liquid

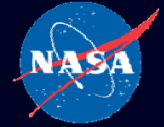
It is well-known that acidic media can dissolve metal oxides such as those comprising lunar regolith (except for silicon dioxide). The net chemical reaction is:



Note that water is produced in this reaction.

Common mineral acids that might be used for such purposes such as sulfuric, hydrochloric, hydrofluoric, etc. present obvious safety and handling issues for space-based applications.

Because of their design flexibility ILs can be made strongly acidic and thereby capable of solubilizing lunar regolith. However, they are less volatile and far less corrosive than conventional mineral acids.



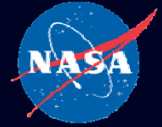
## Electrolysis of Water from Solubilized Regolith

Ionic Liquids have been used with great success as electrolytes. Their wide electrochemical windows (5-6V) make them ideal for applications such as electro-winning of metals.

Once the lunar regolith has been solubilized, the next step is to electrolyze the water produced to generate hydrogen and oxygen. This can be approached in two ways:

- *In-situ* electrolysis, generating oxygen at the anode and hydrogen and/or metals at the cathode.
- Distillation of water from the reaction mixture, followed by electrolysis (using an IL electrolyte) to generate oxygen and hydrogen.





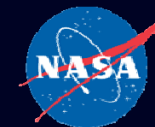
## Regeneration of Ionic Liquid

Because of up-mass costs, it is critical that the IL medium can be regenerated so that the process is economically viable.

During solubilization of the lunar regolith, only the  $H^+$  of the IL acid medium is consumed; the “frame” of the IL and the counter-anion should remain intact. Hence regeneration of the medium essentially consists of re-protonating the IL.

This can be accomplished by electrolysis using a hydrogen gas electrode (a blackened Pt electrode in a hydrogen atmosphere) to oxidize the hydrogen by-product from the water electrolysis step to  $H^+$  at the anode. At the cathode, the metallic ions in solution become reduced to the free metals.:

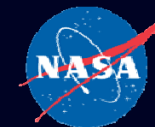




## Solubilization Experiments with JSC-1

Several IL acid systems have been prepared in our laboratory and tested for their abilities to solubilize JSC-1. Initial experiments consisted of taking small (1g) samples of JSC-1 and heating them with aqueous solutions of the ILs for 24 hours. Aqueous solutions were used instead of the neat (anhydrous) ILs so that solubilization would take place at a reasonable rate. Water is needed at the start of the reaction in order to ionize the acid and to act as a stabilizing ligand by coordinating to the metallic ions in the solution.





## Results of Solubilization Experiments

IL Acid	Acid Strength	Ligand	Temperature	Time	Solubilization Efficiency
1-methylimidazolium hydrogen sulfate	weak	water	120°C	4 days	52%
1-methylpyrrolidinium hydrogen sulfate	weak	water	120°C	4 days	49%
3-[butyl-4-sulfonic acid]-1-methylimidazolium hydrogen sulfate	strong	water	120°C	4 days	71%
3-[butyl-4-sulfonic acid]-1-methylimidazolium triflate	strong	water	120°C	4 days	72%
sulfuric acid	strong	water	120°C	4 days	70%

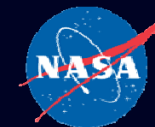


## Results of Solubilization Experiments (cont'd)

Solubilization efficiencies were calculated based on the ratio of the mass of JSC-1 actually solubilized to that theoretically expected to be solubilized (based on the known composition of JSC-1). The results are expressed as percentages.

As seen from the table, the weak IL acids showed solubilization efficiencies around 50%, whereas the strong IL acids showed efficiencies around 70%. This result is not unexpected since stronger acids would be expected to react more effectively than weak acids.

A control experiment using sulfuric acid also showed an efficiency of 70%. This is not surprising since in aqueous solution the strong IL acids are of approximately the same strength as sulfuric acid.



## Composition of Lunar Regolith

Oxide	JSC-1 wt %	st. dev.	mol. wt.	Oxygen Wt. %		lunar 14163 wt. %	mol. wt.	Oxygen wt. %
SiO <sub>2</sub>	47.71	0.1	60.08	25.41		47.3	60.08	25.19
TiO <sub>2</sub>	1.59	0.01	79.87	0.64		1.6	79.87	0.64
Al <sub>2</sub> O <sub>3</sub>	15.02	0.04	101.96	7.07		17.8	101.96	8.38
Fe <sub>2</sub> O <sub>3</sub>	3.44	0.03	159.69	1.03		0	159.69	0.00
FeO	7.35	0.05	71.84	1.64		10.5	71.84	2.34
MgO	9.01	0.09	40.3	3.58		9.6	40.3	3.81
CaO	10.42	0.03	56.08	2.97		11.4	56.08	3.25
Na <sub>2</sub> O	2.7	0.03	61.98	0.7		0.7	61.98	0.18
K <sub>2</sub> O	0.82	0.02	94.2	0.14		0.6	94.2	0.10
MnO	0.18	0	70.94	0.04		0.1	70.94	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.04	0	152	0.01		0.2	152	0.06
P <sub>2</sub> O <sub>5</sub>	0.66	0.01	141.94	0.37		---	141.94	0
oxygen wt. % (silicon dioxide)				25.41				25.19
oxygen wt. % (metal oxides)				18.19				18.79
total oxygen wt. %				43.60				43.98



## Dissolution of Silica in Regolith

Based on analysis of samples from the Apollo missions, it can be seen that approximately 25% of the mass of lunar regolith (and JSC-1) is silicon dioxide (silica), while just under 19% is metal oxides. Hence it would significantly enhance the efficiency of the oxygen extraction process to find a reagent that can solubilize the silica as well as the metal oxides.

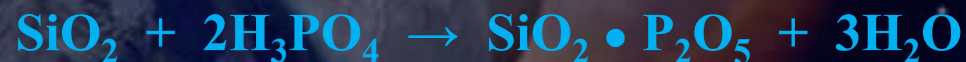
Although acids react with most metal oxides, they do not generally react with silica. Hydrofluoric acid is an exception, but the extreme hazards associated with it make it unacceptable for use on a lunar outpost. Strong bases such as sodium or potassium hydroxide can also react with silica, but they do not react with all of the metal oxides.



## Use of IL/Phosphoric Acid Systems

A benign reagent that is capable of solubilizing silica is phosphoric acid. Phosphoric acid is far less corrosive than acids such as sulfuric, hydrofluoric, etc.; it is non-volatile, and it has low toxicity.

Despite the fact that it is a weaker acid than sulfuric, hydrochloric, or strong IL acids, at high temperatures (150 - 300°C) phosphoric acid reacts with silica and most metal oxides. Phosphate, like water, is a good ligand and coordinates with many metallic ions. The reaction with silica can be shown as:



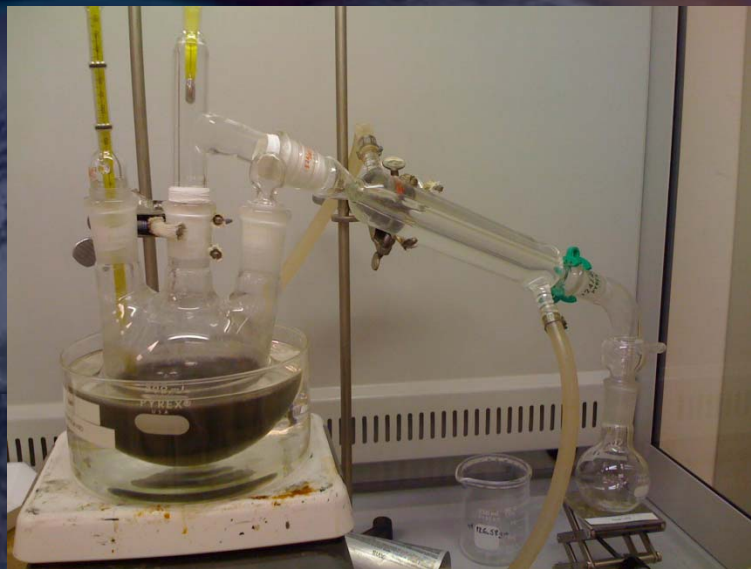
The product of the reaction is silicon phosphate, which remains in solution if the temperature is not too high.

The challenge is to find suitable combination of ILs and phosphoric acid for solubilizing lunar regolith with very high efficiency.

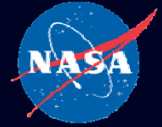


## Solubilization of JSC-1 in IL/Phosphoric Acid

Solubilization experiments were carried out at 150°C on both small (1g) and large (50g) scales with JSC-1 using IL/phosphoric acid mixtures. In both cases, based on the amount of water produced, we estimate that approximately 70 - 75% of the simulant reacted.





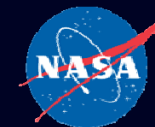


## Analysis of Solubilized JSC-1

Elemental analysis of the solubilized JSC-1 was conducted using Inductively Coupled Plasma techniques.

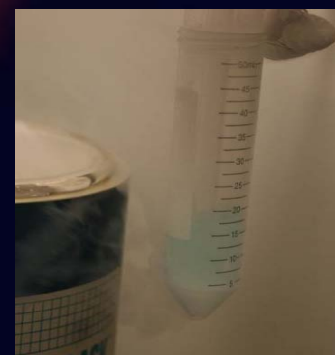
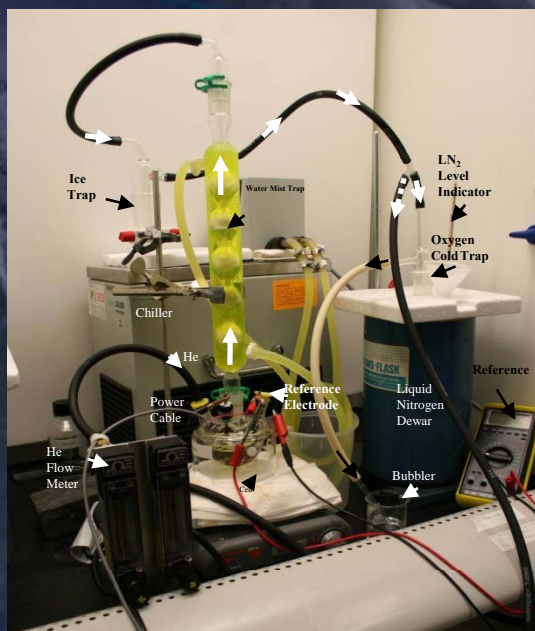
Element	Al	Ba	Ca	Cr	Fe	Mg	Mn	Si	Ti
ppm	3015	29	2869	13	3235	2216	58	1500	435

The results show that, with the exception of silicon, the elemental composition of the solution closely follows that of the starting JSC-1. It should be pointed out that this analysis only identifies species that are in solution; it is possible that some of the JSC-1 reacted with the IL acid medium and formed insoluble products.



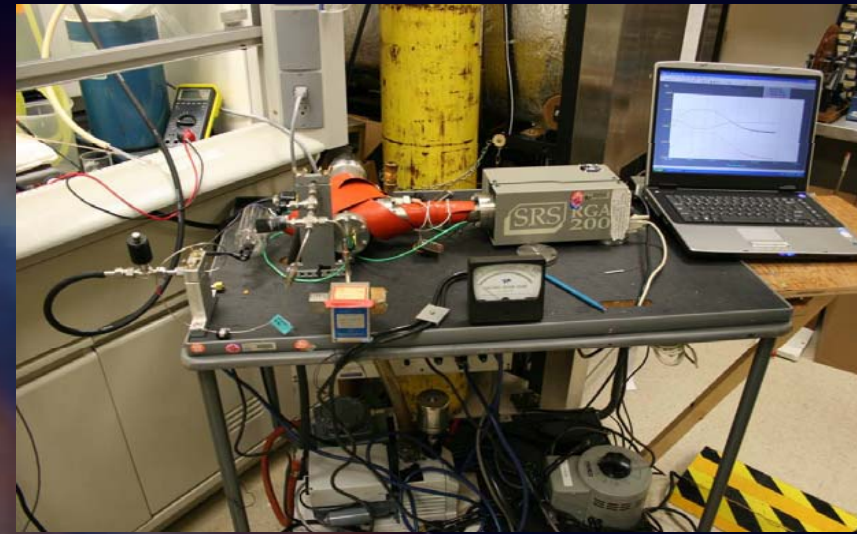
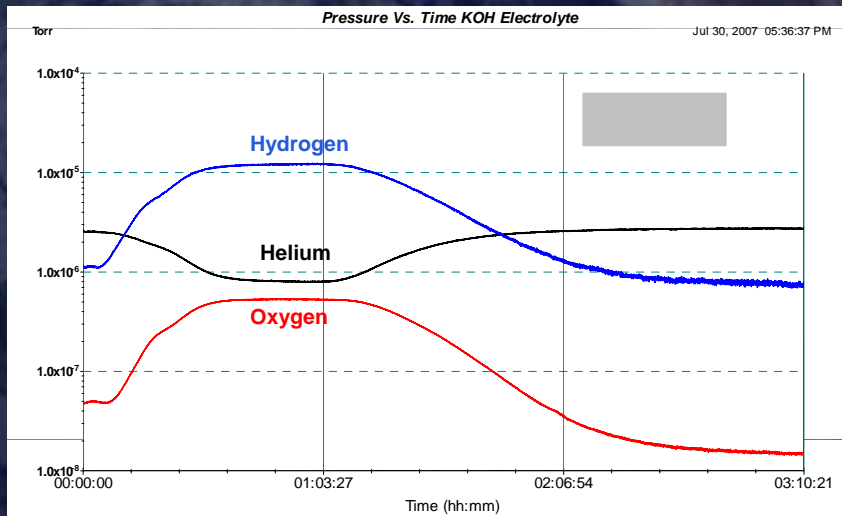
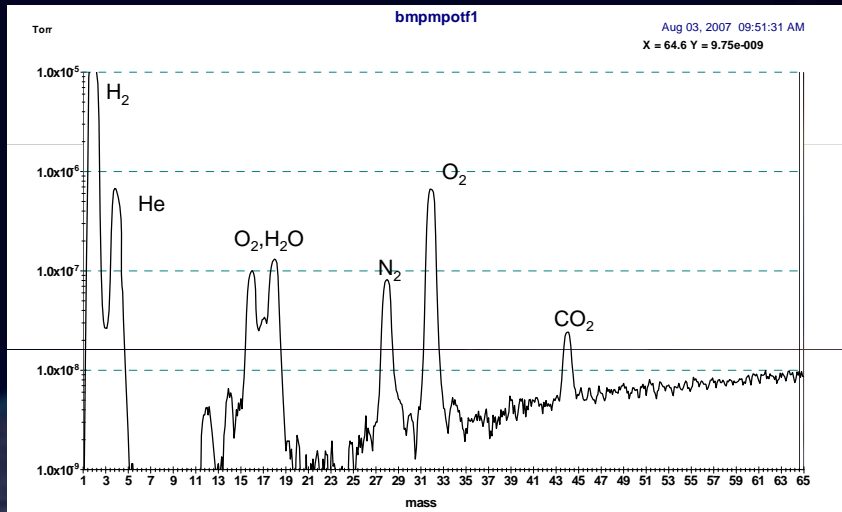
## Water Electrolysis in Ionic Liquid

Electrolysis of the water produced from solubilization of JSC-1 was carried out using an IL electrolyte. The oxygen produced from this reaction was collected and liquefied using an LN<sub>2</sub> bath. Based on the input current and the time of reaction, the efficiency of oxygen collection was determined to be around 80%.





# Residual Gas Analyzer (RGA)



RGA, a small mass spectrometer, was used to analyze gases coming from electrolysis of water. Helium was used as carrier gas and Nitrogen and  $\text{CO}_2$  are background gases from air. RGA can also detect degeneration of IL, if present.



## Ionic Liquid Regeneration Experiments

It is critical that the spent IL acid medium can be regenerated. As a 1<sup>st</sup> step a preliminary experiment was carried out to ascertain whether the IL survives the regolith solubilization process and can be re-protonated.

1g of JSC-1 was reacted with aqueous IL acid, and the insoluble residue was filtered out. The spent acid was run down an ion-exchange column ( $H^+$  form), the eluent was collected, and the water removed. The mass of recovered IL acid was approximately 97% of the starting mass, indicating that the IL does indeed survive the solubilization conditions.

This solubilization experiment was then repeated 4 more times using the recovered IL acid with fresh JSC-1 (1g); in each case the recovery yield was 95 - 98%. These results are very encouraging because they show that the IL can, in principle, be regenerated multiple times. The next (and most technically challenging) step in this research is to conduct regeneration (re-protonation) experiments using a hydrogen gas electrode.



## Conclusions

- Initial results indicate that ionic liquids are promising media for the extraction of oxygen from lunar regolith.
- IL acid systems can solubilize regolith and produce water with high efficiency.
- IL electrolytes are effective for water electrolysis, and the spent IL acid media are capable of regeneration.



## Future Work

- Future work will focus partly on investigating additional ILs with the goal of finding the optimum system for regolith solubilization.
- A significant part of the work will be on electro-chemical regeneration of the IL medium using the hydrogen gas electrode.
- Control experiments will be carried out using standard solutions containing the individual metallic ions present in solubilized regolith.