

Analysis of Lunar Non-Water Volatiles and Processes for their Separation and Utilization

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In-situ resource utilization (ISRU) has been proposed for processing water-ice on the Moon to provide fresh water, breathable oxygen, and rocket propellant for future exploration missions. On the Moon, evidence of water-ice has been detected in permanently shadowed regions (PSR) concurrently with other non-water volatile (NWV) species. All resources on the Moon can have utility in a lunar economy and some may have high enough value to warrant the expense of developing and deploying systems to process and utilize them. At the same time, some NWVs pose significant threats to the lifetime of ISRU systems and related equipment. As an example of one potentially high-value resource, ammonia that is co-located with lunar water-ice could be used as a refrigerant, as a fuel cell consumable, as fertilizer, as a feedstock for hydrazine production, or as a source of make-up nitrogen for lunar habitats. As an example of a hazardous NWV, mercury can cause leaching and corrosion of metals from plumbing and components and is a known toxin to humans. In this paper, we describe and analyze the lunar NWV landscape through the lens of potential value and risks associated with the NWVs detected to date. Technology concepts for processes to separate and utilize these NWVs are defined, modeled, analyzed, and traded. As a result of these efforts, key research and development gaps are identified for future investment. Because Paragon Space Development Corporation has been developing technologies for the capture, purification, and utilization of lunar water, ISRU architectures are also presented where these capture and utilization technologies for NWVs can be integrated or interfaced with other relevant systems.

Nomenclature

| | | | |
|----------|--|------------|--|
| CH_4 | = Methane | $LCROSS$ | = Lunar Crater Observation and Sensing Satellite |
| C_2H_4 | = Ethylene | LRO | = Lunar Reconnaissance Orbiter |
| CH_3OH | = Methanol | $mol\%$ | = molar percentage |
| CO | = Carbon monoxide | N_2 | = Nitrogen |
| CO_2 | = Carbon dioxide | $NASA$ | = National Aeronautics and Space Administration |
| $DWSIM$ | = Dynamic Sequential Modular Chemical Process Simulator | NH_3 | = Ammonia |
| H_2 | = Hydrogen | NWV | = Non-Water Volatile |
| H_2O | = Water | O_2 | = Oxygen |
| H_2S | = Hydrogen sulfide | P_{H_2O} | = Partial pressure of water vapor |
| Hg | = Mercury | P_x | = Partial pressure of component x |
| $ICICLE$ | = ISRU Collector of Ice in a Cold Environment | PSR | = Permanently Shadowed Region |
| $IHOP$ | = ISRU-derived water purification and Hydrogen Oxygen Production | SO_2 | = Sulfur dioxide |
| $ISRU$ | = In-Situ Resource Utilization | T | = Temperature |
| IWP | = Ionomer-membrane Water Processing | TCS | = Thermal Control System |
| | | TRL | = Technology Readiness Level |

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I. Introduction & Background

In-Situ Resource Utilization (ISRU) of water in regolith on the Moon has long been proposed by NASA as a means of generating potable water, breathable oxygen, and rocket propellant (both fuel and oxidizer) to support human presence on and in the vicinity of the Moon. Since the success of the Lunar Crater Observation and Sensing Satellite (LCROSS) mission, the water-ice in Permanently Shadowed Regions (PSR) in polar lunar craters has been estimated to be distributed in regolith at concentrations of $5.6 \pm 2.9\%$ by mass^{1,2}. In addition, the LCROSS mission detected the presence of other chemical species at concentrations shown in Table 1.^{††}

Many extraction methods of the lunar ice have been proposed in recent years^{3,4,5,6,7,8,9} and are undergoing active investigation. In each of these lunar water utilization architectures, heating water in a lunar vacuum (or slightly pressurized, ~ 100 's Pa) environment to drive sublimation is the primary step used to liberate the water from regolith. By extension, it becomes necessary to re-collect the water vapor either via condensation or desublimation (deposition), which itself already incurs an energy penalty in the form of needing to reject heat from the water collection process. Based on the LCROSS data, a considerable load of non-water volatiles (NWVs) is expected to be present with alongside water-ice in PSR processing streams and most, if not all, will need to be removed from water before it can be used in downstream systems. Therefore, there is an identified need for both collection and purification of water from lunar ice sources.

To meet this ISRU community and NASA-identified need, Paragon and our partners have been developing and testing key components and assemblies for ISRU water processing and purification described in previous ICES papers^{10,11,12,13,14}, including the ISRU Collector of Ice in a Cold Lunar Environment (ICICLE) Cold Trap for simultaneous water collection and purification via “freeze distillation” and the ISRU-derived water purification and Hydrogen Oxygen Production (IHOP) system for potable water purification and H_2 / O_2 generation via specialized membrane distillation. In this work it has been identified that certain NWVs in the LCROSS volatiles data set may pose hazards to ICICLE and IHOP, such as mercury (Hg) causing corrosion or ammonia and sulfur compounds interacting in the gas phase to form salt precipitate aerosols. Consequently, Paragon has now studied the potential to both separate and utilize these hazardous NWVs in a project entitled “Ammonia and Volatiles Accumulation in Lunar Architecture for non-Water Capabilities furthering Human Exploration,” or AVALANCHE. The present work describes the AVALANCHE investigation into NWVs utilization to create a more-complete ISRU architecture per Figure 1.

Table 1. Water and NWVs Detected in Lunar Regolith.

| Volatile | LCROSS [†] Molar Ratios (mol per mol $H_2O \times 100\%$ (mol%)) | Mass % in Regolith | NWV kg per kg H_2O | NWV kg per 225-day period at 2.8 kg/hr H_2O rate |
|------------------|---|--------------------------|----------------------------|--|
| Hydrogen Sulfide | 7.30 | 0.77 | 0.14 | 2089 |
| Ammonia | 2.66 | 0.14 | 0.026 | 386 |
| Sulfur Dioxide | 1.40 | 0.28 | 0.05 | 753 |
| Ethylene | 1.37 | 0.12 | 0.02 | 323 |
| Methane | 0.28 | 0.01 | 0.003 | 39 |
| Methanol | 0.67 | 0.07 | 0.046 | 182 |
| Carbon Dioxide | 0.94 | 0.13 | 0.023 | 348 |
| Mercury | 0.36 | 0.22 | 0.04 | 606 |
| [Water] | 100 | 5.6 | - | [15,120 kg] |

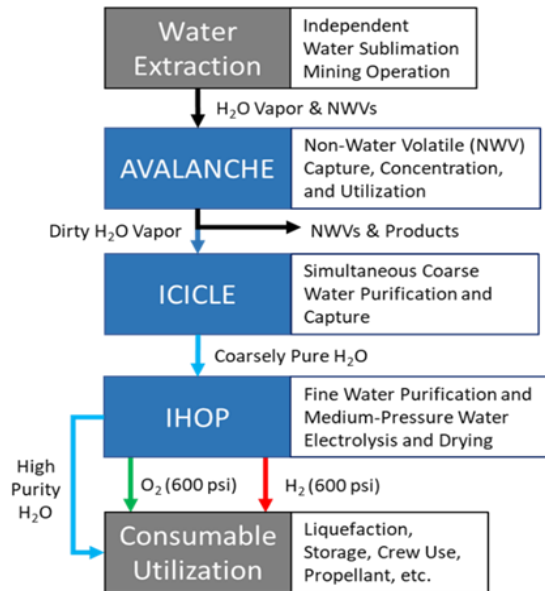


Figure 1. Paragon's ISRU Architecture

^{††}In previous work^{10,12,14}, Paragon estimated the concentration of H_2 and CO from Gladstone et al.² and included it with estimates for volatiles described by Colaprete et al.¹ However, work by Hurley et al. in 2012¹⁵ and more recently 2023¹⁶ describing uncertainties related to the detection and derivation of abundances of these compounds make it challenging to arrive at an engineering estimate of their concentration with respect to water in lunar regolith. They have been omitted from analysis and results in this paper so as not to unintentionally mislead readers.

II. Non-Water Volatiles of Interest

The following research stemmed from the expectation that lunar ice mining will generate non-water volatiles that will be present in the water vapor stream generated by auger drills, thermal corers, or other methods of water-ice extraction. The best (current) available source of information for what constituents may be present in the vapor generated by these devices is from the LCROSS mission, which sent a “kinetic impactor” to impact the surface of the Moon at the Cabeus crater. The crater was chosen partially because portions of it are a PSR, the environment in which we expect the most water-ice to be present around the Lunar south pole. For reference the Cabeus crater has an average temperature around 100 K and is thought to be comprised of mostly lunar highlands soil type. This impact reached ~1000 K and ejected a plume into the Lunar exosphere whose spectra was measured by the Lunar Reconnaissance Orbiter. This in turn led to in-depth spectral analysis of the ejected plume and an assessment of the constituents in the plume. The assessment has faced scrutiny for its wide uncertainty band due to both the measurement methodology and the temperature at which the impact took place, which almost certainly changed how chemicals were bonded to each other in the regolith. More information on the experiment can be found in the references.^{1,2,15,16} The pertinent results of this work are summarized in Table 1, which contains the molar ratios of gaseous volatiles compared to that of water and contains the percent mass expected of the volatiles in the regolith. Note the wide uncertainty bands on the water and therefore on the other constituents as well; this work focuses on the expected averages, but future work will include the full uncertainty propagation and quantify impacts due to higher or lower NWV concentrations.

In summary, the majority of research and trades done to understand and manage icy non-water volatiles that will be present on the Moon is rooted in the LCROSS data as a sole point of truth. Using the LCROSS data, we can predict with some reasonableness the constituents in a vapor stream generated by a lunar ice mining system. Geologic analysis of the Apollo missions provides more information on other gases and vapor-mobilized elements that may be present (e.g., sulfur), but uncertainties in the analysis and lack of temperature-dependent data makes understanding the exact makeup of the gas stream coming from a notional ice extraction method extremely challenging. Therefore, processing equipment and solutions should be generally robust to a wider range of chemicals and constituents to ensure operability in the lunar environment, with special focus on the constituents found in Table 1 until better ground-truth data can be gathered from upcoming missions such as VIPER and PRIME-1.

Some of these NWVs found in the regolith are of particular interest for separation. Mercury (Hg) will degrade downstream equipment over time and if captured with water will necessitate additional processing steps, as it is highly toxic and reactive^{17,18}. Gaseous ammonia (NH₃) and sulfur dioxide (SO₂) have several chemical reactions which result in the formation of ammonium sulfate (NH₄)₂(SO₄) and ammonium sulfite, (NH₄)₂(SO₃), salt precipitates which will spontaneously precipitate in the stream¹⁰ and will get caught in any cold trap technology attempting to capture water (including ICICLE) unless there is a sufficient mitigation strategy in place. They are corrosive to steels and aluminums,^{19,20} and are difficult to remove from liquid water. On the more positive side, these salt precipitates can potentially be used in other ISRU products, such as fertilizer, or could be broken back down into ammonia for the variety of useful products that can be generated from it (refrigerant, fuel cells). Focusing on these constituents, a few process architectures were proposed to separate and handle (dispose of or use in products) the NWVs. The following processes were evaluated with regards to each identified constituent (Table 2):

Table 2. Separation or handling methods for select NWVs and their potentially useful outputs.

| Constituent | Separation or Handling Method(s) | Useful Output(s) or Result(s) |
|---|--|---|
| Mercury | Cold trapping, sorbents, photochemical oxidation | Less/no mercury in water processors, extended hardware life |
| NH ₄ Salts (in stream) | Gravity sedimentation, cyclonic separation, filtration | Less/no ammonia or sulfur in water processors |
| Dust/Dirt Solids | Gravity sedimentation, cyclonic separation, filtration | Less/no dust in water processors, extended all-around hardware life |
| CH ₃ OH+SO ₂ +NH ₃ +H ₂ S | Cold trapping exhaust from primary (water) trap | Collected NWVs & residual water |
| NH ₄ Salts (separated out) | Thermal decomposition, integrate into fertilizer | Raw ammonia, fertilizer for soil |
| Raw Ammonia (from separated salts) | Mole sieving, gas scrubbing, thermal decomposition | Purified ammonia, H ₂ , and/or N ₂ , stabilized fertilizers |

The separation and handling of each constituent to either prevent damage to an existing component or create an opportunity for additional resource utilization can be framed as a series of architectural “stages”, which are summarized into Figure 2’s flow charts to illustrate the variety of lunar water vapor processing architecture options possible by utilizing different parts of the above list. All of the options assume that the baseline water-based ISRU architecture is maintained, where there is 1) a sublimation ice mining system, 2) a cold trap water vapor capture system, and 3) a water processor which converts the captured water into potable water, hydrogen, or oxygen. This study does not investigate alternative core ISRU architectures such as oxygen-from-regolith, though the outlet streams of other architectures are expected to still include volatiles that will require separate processing stages.

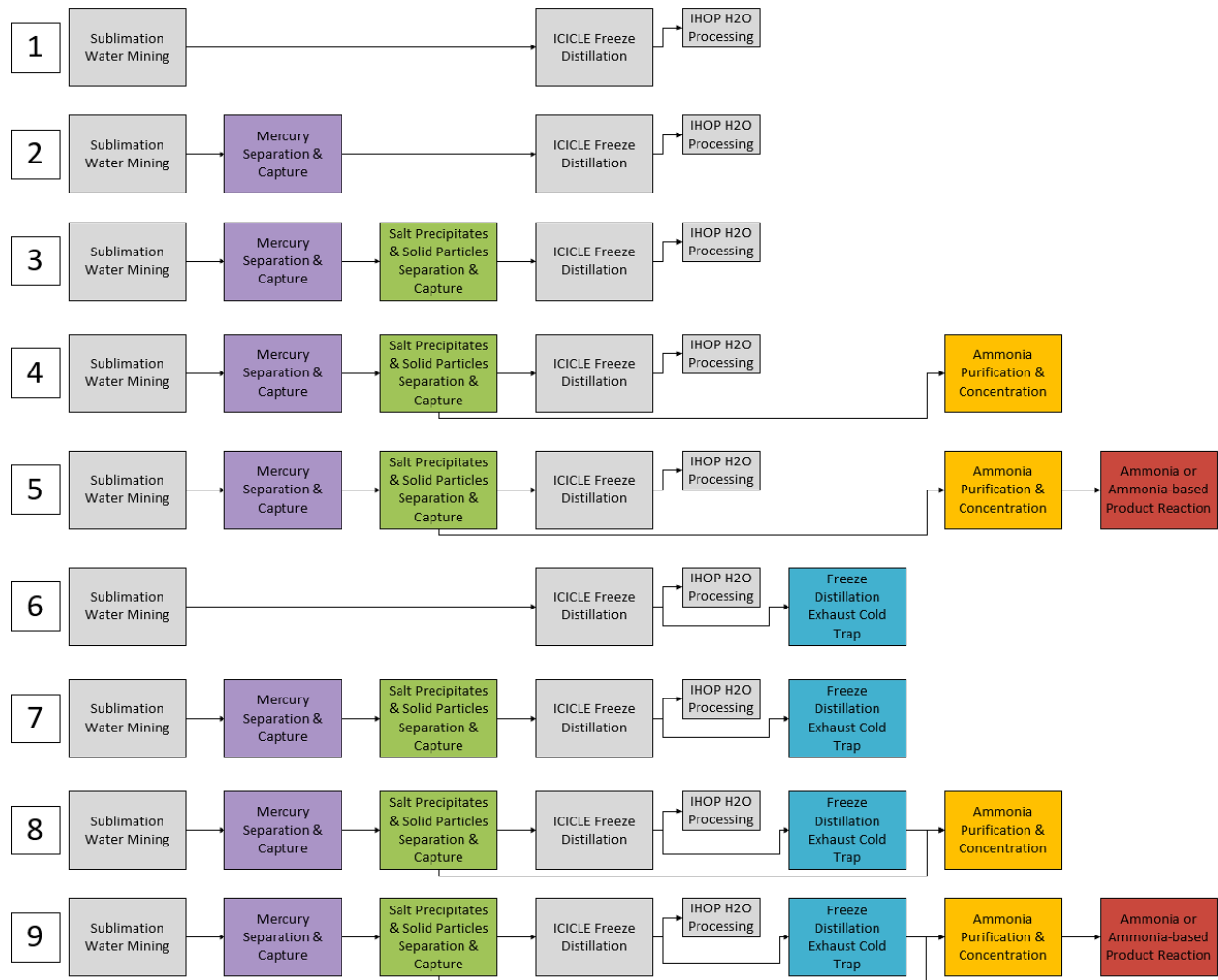


Figure 2. AVALANCHE NWVs architectural options flow chart. Gray boxes were investigated as part of other work. Chart is ordered in terms of described processes and approximate complexity, not necessarily preference nor viability.

III. Architecture Refinement

For each of the above proposed steps, a research assessment was conducted to evaluate the cost-benefit of separating out the particular constituent from the stream and/or later utilizing it in some way. The resulting cost-benefit

assessment for the capture and separation steps is summarized in Figure 3. None of the assessed capture / separation stages had specific negative consequences to the downstream architecture (besides the obvious increase in overall mass and complexity that is true universally for all process additions). In terms of benefits, the removal of mercury and ammonia-sulfur salts from the vapor stream showed strong potential benefits to the overall architecture and had at least one feasible path to accomplishing the separation stage. Dust removal and capturing additional NWVs in a cold trap on the exhaust of ICICLE were less valuable or feasible. These are each described further below.

| Process | Effects on Other Equipment | | | | | |
|-------------------|----------------------------|---|----------------|--------|------|-------------------|
| | Mercury Removal | Salt Removal | Solids Removal | ICICLE | IHOP | Exhaust Cold Trap |
| Mercury Removal | X | | | | | |
| Salt Removal | X | X | | | | |
| Solids Removal | X | X | X | | | |
| ICICLE | X | X | X | X | | |
| IHOP | X | X | X | X | X | |
| Exhaust Cold Trap | X | X | X | X | X | X |
| Legend: | X | Not applicable | | | | |
| | | Certainly feasible and valuable to overall architecture | | | | |
| | | Potentially feasible and valuable to overall architecture | | | | |
| | | Positive effect on downstream equipment | | | | |
| | | No effect on downstream equipment | | | | |
| | | Negative effect on downstream equipment | | | | |

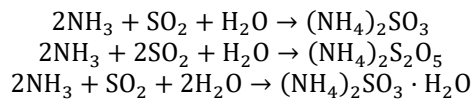
Figure 3. Effects of capture and separation stages on each other.

A. Mercury Removal

Due to its extreme toxicity, mercury poses a high risk and must be removed at some stage in the water processing architecture. Since mercury has interactions with most metals^{17,18} and is more difficult to separate from liquid water than from water vapor, it makes simple logical sense to remove mercury as soon as possible, and especially upstream of the water-depositing cold trap assembly (ICICLE, in Paragon’s architecture) where it will condense and get trapped with the water-ice. Removing mercury at the beginning stages of the process stream also limits any material changes necessary for downstream components that may not have considered the presence of mercury in their original designs.

B. Salt Precipitates Removal

The ammonium sulfate and ammonium sulfite salts, formed in the reaction of ammonia and sulfur dioxide in the process stream, are also corrosive to steel and aluminum in the presence of water,^{19,20} meaning they would damage the water-ice cold trap and potentially the water processor. These reactions are complex, but the properties of these sulfite salts are largely the same and can be handled together. The precipitation reactions happen spontaneously and rapidly ($t_{residence} \sim 30$ seconds) if all three components are present and the temperature is kept sufficiently low. Each precipitation reaction is exothermic with (counterintuitively) decreasing reaction rates at higher temperatures, so active temperature control is required to maintain high conversion efficiency. The three reactions are the formation of (in order) ammonium sulfite, ammonium metabisulfite, and ammonium sulfite monohydrate:



These salts will form in a roughly 68:30:2 split (% by mass) in the nominal lunar vapor stream process conditions of ≤ 293 K and an NH_3/SO_2 mole ratio of 2 with high water content. Keeping the flow colder increases the conversion efficiency, with ammonia and sulfur dioxide conversion efficiencies near 90% at 283 K. More specifically, our thermodynamic model based on literature data²¹ predicts that given the expected composition of the flow stream, salting will consume 92% of the ammonia, 87% of the sulfur dioxide, and 1.2% of the water vapor at 283 K. These salts are soluble in water at this and higher temperatures and are more difficult to remove from liquid water. If these salts are allowed to continue through the process stream, they will dissolve into the water and will need to be removed via distillation or specific adsorption. This adds additional complexity and equipment need to the liquid water processing system. Removing the salts upstream removes corrosion risk and improves water purity downstream.

C. Dust Removal

If not removed upstream of the cold trap, dust will contaminate the captured water-ice and require filtration to remove it. It may also mechanically abrade and degrade components both upstream the cold trap and downstream in

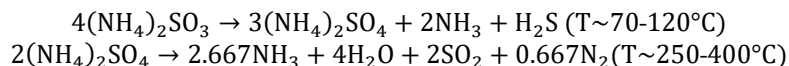
the exhaust. Though the lunar dust is considered a major health hazard, it is not expected to be significantly chemically active within water or water-ice, therefore simple mechanical filtration of the liquefied water after capture is likely sufficient dust mitigation and filtration or capture ahead of the cold trap is useful, but not critical.

D. NWVs Exhaust Capture

It is known NWVs will be vented from ICICLE cold trap exhaust¹², and if these volatiles could be captured then they could (potentially) be utilized for value-added purposes. In the configuration where no mechanical compression step is added, the exhaust cold trap could collect methanol, sulfur dioxide, and ammonia as ices using the same freeze distillation process as ICICLE at a lower temperature. It would also collect any remaining water not captured by ICICLE. If a compression step was added, the partial pressures of the exhaust constituents could be increased to allow capture of hydrogen sulfide and higher collection efficiencies overall. Efficiency of this cold trapping, as well as rejecting the necessary heat, is a concern.

E. Ammonia Purification and Concentration (from salts)

Ammonia has the potential to be used in a variety of end products, such as refrigerant or within fuel cells, but it must first be generated and purified from the captured ammonium salts. The primary way to generate ammonia from these salts is thermal decomposition, though this process is not well understood in the low-pressure and anoxic process environment. Regardless, it is generally agreed upon^{21,22} that thermal decomposition of the sulfite salts will occur within 70 – 120°C, and decomposition of sulfate salts requires much higher temperatures (~250 – 400°C):



Because the decomposition also generates more hydrogen sulfide, sulfur dioxide, and water, a cyclic process may be necessary to generate useful amounts of ammonia; further, the ammonia would then require scrubbing to reach a pure enough state for utility in more sensitive application (fuel cells). The complexity of these processes would make them unfeasible to perform in-situ during collection, so they would instead have to occur at the processing plant on the crater rim, perhaps using waste heat from the hydrogen and oxygen production as a power source. Lastly, if ammonia generation was not sought after, the salts (in particular the ammonium sulfate) could be used as a low-grade fertilizer in their precipitated state. Performing only the first step of decomposition (to convert sulfite to sulfate) could generate a reasonable quantity of fertilizer without necessitating additional ammonia processing steps.

F. Ammonia or Ammonia-based Product Generation

Ammonia recovered from the regolith salts and purified can be used in a multitude of end products, including as a refrigerant, within a solid oxide fuel cell, further decomposed into hydrogen and nitrogen for a proton-exchange membrane fuel cell or buffer gas, or mixed into a more stable fertilizer. However, given the already-challenging process of thermally decomposing the ammonium salts into pure ammonia, it is doubly challenging to purify the ammonia to an extent where it can be reliably used in a fuel cell application or be re-combined into a high-performance fertilizer (such as ammonium nitrate). Both the solid oxide and proton-exchange membrane fuel cells would require substantially more robust purification methods that would quickly take away the benefit of recovering ammonia. That said, utilizing ammonia in an acceptably “dirty” state could still make it effective as a refrigerant (standalone or as an additive).

IV. Architecture Downselection Methods

With the potential concepts defined and ranked qualitatively, a first principles analysis for each separation and processing method was conducted to evaluate the *feasibility* of the technology in the lunar ice mining process and more generally in the lunar environment. The criteria for feasibility included system mass, power or materials consumption, constituent collection efficiency, and controllability. For processes that had well-defined physical relationships, basic process models were created in the DWSIM chemical process modeling software to establish rates and efficiencies of constituent capture at lunar process conditions (<1000 Pa, process stream defined by Table 1), as well as define the required heat addition or removal to maintain the process. For example, the feasibility of mercury condensation was first assessed through first principles condensation distillation to determine a collection efficiency, followed by sizing a condensing heat exchanger that could provide sufficient heat transfer to both cool the flow and condense out the mercury volatile. This was successfully performed with the simple DWSIM model shown in Figure 4. Since the condenser was both the lowest mass technology (~1.5 kg for the full-scale application), had good collection efficiency (~97% at 283 K), and required no consumables (just a thermal control system (TCS)) to operate,

it was considered the most feasible of the mercury handling technologies surveyed. In comparison, other mercury-capturing methods (sorbents, oxidation) required significant consumables or oversized support hardware (10's of kilograms for the full-scale application) and were not considered feasible.

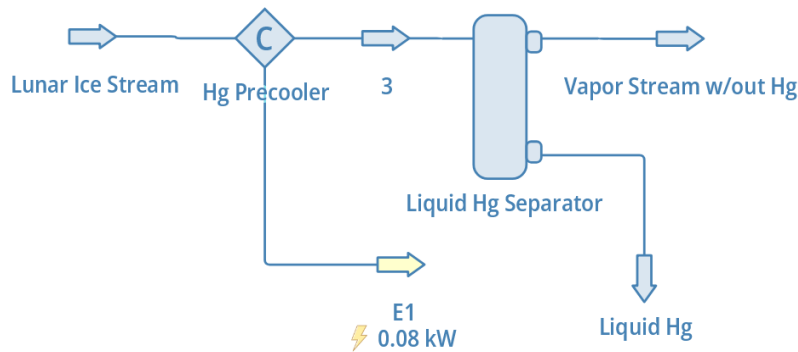


Figure 4. Simple DWSIM model for mercury condenser sizing.

Those technologies that were determined as feasible were then evaluated for their *value*. This was accomplished by determining sources of valuation for each process including value of the constituent recovered, value of removing the constituent in the process, and value of the utilization of the constituent in a further process. Basic system design and sizing was conducted for feasible technologies to ascertain their impact on total plant mass and performance as a function of plant size, and to determine at what point the technology “pays for itself” by adding more value than it required to incorporate. An example of the mass and breakeven time assessment is given in Figure 5 for the ammonium salts generation and separation processes, for which a cyclone separator was determined the most feasible option (again, for being by-far the most mass and volume competitive technology of those surveyed from Table 2). Observe that because most of these technologies require temperature control, increases in required support TCS typically offset the mass savings from increasing the scale of the capture technology.

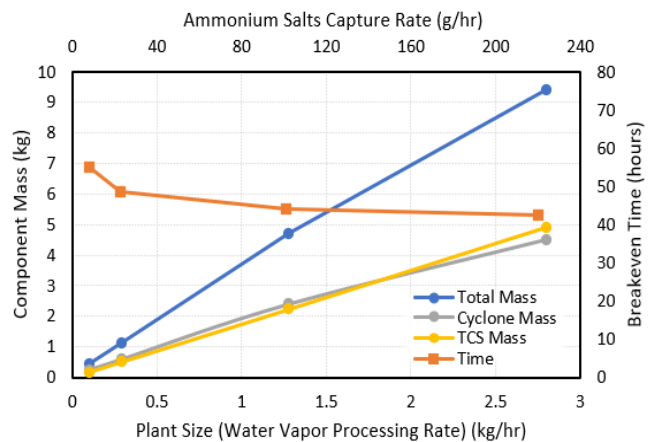


Figure 5. Comparison of cyclone separator’s component mass and breakeven time as a function of ISRU propellant plant size. Breakeven time is defined as the operating time required for captured useful constituent mass to exceed launch mass of component.

The feasibility and value studies were repeated for every identified separation and capture method, ammonia decomposition method, and ammonia product generation method identified. For brevity, only the results of this study are included in this paper.

On the capture side of the architecture, the list of *feasible* architecture options includes:

- Mercury removal from the stream via a temperature-controlled condenser with a liquid trap
- Cooling of the flow to allow salt generation, and subsequent removal of the salts via a cyclone separator
- Removing dust with the cyclone separator
- Capture exhaust from the ICICLE cold trap to retain methanol and water

Of these options, all but the exhaust cold trap have a clear value-add to the architecture. Each component not only recovers a resource, but also limits the exposure of downstream components (ICICLE, IHOP) to hazardous and/or lifetime degrading constituents. If salt capture is performed, at least some dust removal happens as a “free” consequence. The exhaust cold trap is limited in its effectiveness, and only trades well on a mass and required support TCS basis if it captures only methanol and water from the exhaust of the primary cold trap. This downselected architecture was also developed in DWSIM as a combination of all the aforementioned models, with Table 3 showing the predicted collection efficiencies after each stage in the architecture if all of them are implemented.

On the production side of the architecture, the list of *feasible* options includes:

- Thermal decomposition of the captured sulfite salts into ammonia and ammonium sulfate
- Purification of the ammonia by removing known contaminants (Hg, H₂S)
- Usage of Ammonia as a refrigerant recharge
- Usage of Ammonium Sulfate directly as a fertilizer
- Usage of Ammonia in a solid-oxide or proton-exchange membrane fuel cell as a weight-efficient source of power

Table 3. Predicted process collection efficiency summary.

| Temperature: | 283 K | 283 K | * | 170 K |
|--|-------------------|----------------|---------------|-------------------|
| Collection Efficiencies at each Stage: | Mercury Separator | Salt Separator | ICICLE | Exhaust Cold Trap |
| Hydrogen sulfide | 0% | 0% | 0% | 0.51% |
| Ammonia | 0% | 91.72% | 0% | 0.33% |
| Sulfur dioxide | 0% | 87.13% | 0% | 1.64% |
| Ethylene | 0% | 0% | 0% | 0% |
| Methane | 0% | 0% | 0% | 0% |
| Methanol | 0% | 0% | 0% | 99.13% |
| Carbon dioxide | 0% | 0% | 0% | 0% |
| Mercury | 99.47% | 0.52% | 0% | 0% |
| Water | 0% | 1.22% | 94.98% | 3.65% |

Of these, the most value-added are those that can use or manipulate ammonia in forms that are easily accessible or generate the most direct benefit. In other words, decomposition of the ammonium sulfite into ammonia and ammonium sulfate and then usage of each product in a simple application such as refrigerant and fertilizer is the ideal architecture, especially for early lunar plant operation and/or early human presence on the Moon.

*Number intentionally not published. NWV collection efficiencies of ICICLE are in the 0.001% range, per both this work's DWSIM model and prior work's analysis¹⁰.

V. Recommended Approach for Handling Non-Water Volatiles

Using the information gained from the feasibility and value studies, Paragon ranked the proposed technologies and process steps both qualitatively and quantitatively based on both feasibility and value and arrived at a downselected architecture with potential for the highest value and lowest complexity based on our technical assessment. The processes selected as the most viable and value-added to the lunar ice processing plant architecture are:

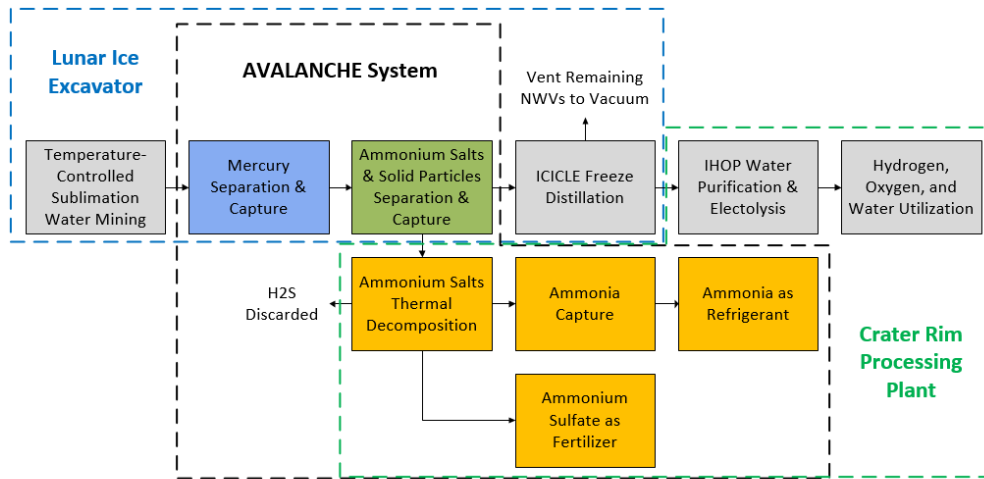
- Mercury separation and capture via condensation
- Salts separation and capture via temperature-controlled cyclonic separation
- Thermal decomposition of the ammonium salts into:
 - a. Ammonia to be purified, captured, and used as a refrigerant recharge or supplement
 - b. Ammonium sulfate to be used as a basic fertilizer
- Dust particulates and secondary solids capture via the same cyclonic separation used for salts

The processes *not* selected for further investigation for lunar ice processing plant architecture were:

- Mercury capture through sorbents or oxidation
- Salts (or dust) separation and capture via simple gravity-based sedimentation
- NWV exhaust capture via colder-than-ICICLE freeze distillation
- Further product-reacting of ammonia for use, including:
 - a. Conversion into ammonium nitrate (modern) fertilizer
 - b. Reaction within a solid-oxide fuel cell
 - c. Cracking into H₂ and N₂ for use as gas or within a proton-exchange membrane fuel cell

Ultimately the downselected architecture of the trade study is Path 4 of Figure 2, with some consideration for the usage of ammonia based on near-term and far-term ISRU needs. The most critical steps to add to the baseline architecture (Path 1) are the Mercury Separation & Capture and the Salt Precipitates & Solids Separation & Capture. These two steps have the most direct value in supporting downstream water / propellant processing equipment. The ammonia processing stages should be added to later, more-developed lunar processing plants, as their value is centered around generating ammonia-based products which will be only valuable when used to help sustain human presence. Figure 6 outlines this recommended architecture, showing the near-term additions as integrated within the lunar ice excavator alongside the thermal miner and ICICLE and the far-term additions as part of the crater rim processing

plant. The DWSIM model confirms performance of these individual stages and provides confidence that the process steps can occur in-sequence successfully with minimal changes to either the thermal ice mining upstream or the ICICLE freeze distillation downstream.



Grey boxes indicate parts of established lunar ice mining architecture prior to this work

Figure 6. AVALANCHE downselected system schematic in water-ice mining ISRU architecture.

VI. Conclusions & Forward Work

Over the course of the AVALANCHE research project, Paragon has developed a citable set of resources and reference material to define the different architectures that could be viable on the lunar surface for a water and non-water volatiles processing plant. These different potential architectures were reviewed, and a series of potential processes for achieving the goals of mercury separation, salt precipitates/solids separation, NWV exhaust capture, and ammonia product generation were identified. Of these, several processes and technologies were confirmed as technically viable and valuable via analysis and a detailed trade study. The resulting down-selected and recommended architecture includes mercury separation, salt precipitates/solids separation, and straightforward conversion of the salts into ammonia products. For each of these components, Paragon has generated preliminary sizing and collection efficiency estimates so that they can be further evaluated and eventually integrated into a water-ice ISRU system.

At the conclusion of the project, a preliminary test design and accompanying test plans were completed which outline the work required to raise the Technology Readiness Level (TRL) of the selected components in a further-Phase effort. Figure 7 depicts the high-level test design and illustrates how each test section can and will be modularly linked between each other for different test configurations to experimentally assess the architecture's benefits. The plan is comprised of a series of individual process demonstrations (mercury capture, salts capture, salts decomposition) followed by a total system test to understand the interactions of the selected equipment with each other. Supporting experiments to verify fundamental material information and design assumptions have also been planned. A reduced set of LCROSS-derived constituents were identified to use for the test campaign to create representative process flows that simulate the lunar ice mining stream's pressure, temperature, flow rates and composition. A test matrix with the verification and validation methods for each test was derived from overarching test objectives and requirements to ensure each of the proposed components and processes could be raised to TRL 4. Completing this testing will greatly increase the fidelity of the added ISRU components and the robustness of the water-ice ISRU architecture as a whole.

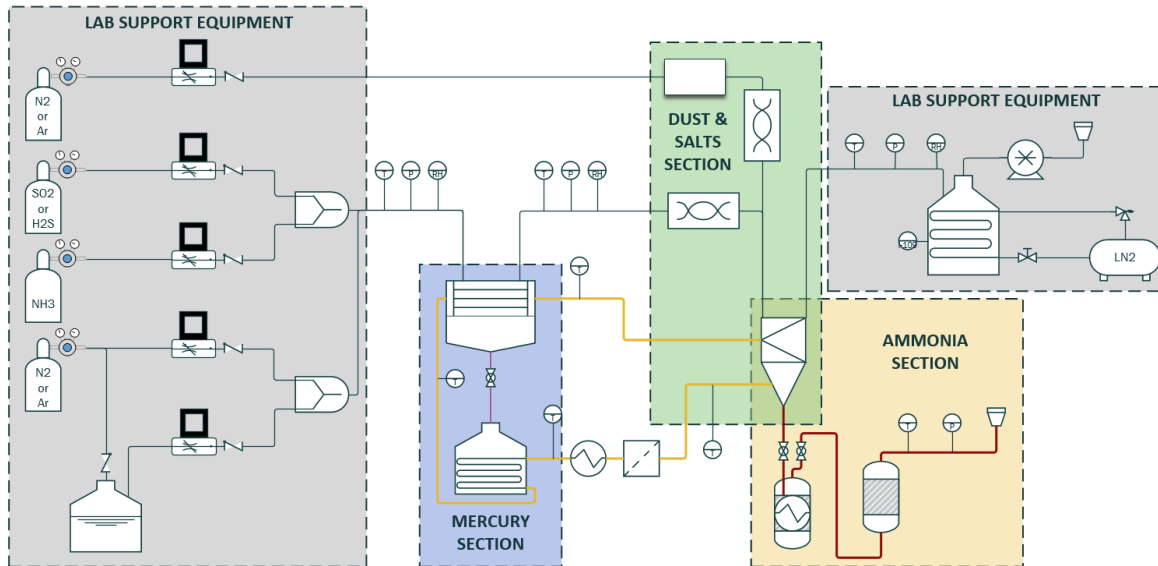


Figure 7. AVALANCHE System Test Schematic Overview

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References

- ¹Colaprete, A., et al., "Detection of water in the LCROSS ejecta plume," *Science*, Vol. 330, No. 6003, 2010. pp. 463-468.
- ²Gladstone, G. R., et al., "LRO-LAMP observations of the LCROSS impact plume," *Science*, Vol. 330, No. 6003, 2010. pp.472-476.
- ³Collins, J. and Araghi, K.R., "Lunar Water Extraction via Lunar Auger Dryer ISRU (LADI)," *Accelerating Space Commerce, Exploration, and New Discovery (ASCEND) Conference*, Oct. 2023, AIAA 2023-4758.
- ⁴Zacny, K., Vendiola, V., Morrison, P., and Paz, A., "Planetary Volatiles Extractor (PVex) for Prospecting and In Situ Resource Utilization," *17th Biennial International Conference on Engineering, Science, Construction, and Operations in Challenging Environments*, Earth and Space 2021, April 2021, pp. 713-723.
- ⁵Sowers, G., "Thermal Mining of Ices on Cold Solar System Bodies," NASA Innovative Advanced Concepts (NIAC) Phase I, Final Report, February 2020.
- ⁶Kuhns, Matthew, Roger J. Kuhns, Forrest Meyan, Philip Metzger, Hunter Williams, and Kris Zacny. "Rocket Mining for Lunar and Mars ISRU." In *Handbook of Space Resources*, pp. 491-520. Cham: Springer International Publishing, 2023.
- ⁷Metzger, P. T., Sapkota, D., Fox, J., and Bennett, N., "Aqua Factorem: Ultra Low Energy Lunar Water Extraction," NASA Innovative Advanced Concepts (NIAC) Phase I, Final Report, March 2021.
- ⁸Sercel, J., "Lunar Polar Propellant Mining Outpost (LMPO): A Breakthrough for Lunar Exploration & Industry," NIAC Phase II, 2020, Award Announcement.
- ⁹Jurado, N. I., "Rarified Water Vapor Deposition from Icy Lunar Regolith on an Engineered Cold Plate," Master's Thesis. The University of Texas at El Paso, 2021.
- ¹⁰Holquist, J.B., Gellenbeck S., Bower, C.E., and Tewes, P., "Experimental Proof of Concept of a Cold Trap as a Purification Step for Lunar Water Processing," *50th International Conference on Environmental Systems*, July 2021, ICES-2021-292.
- ¹¹Holquist, J.B., Gellenbeck, S., Bower, C.E., and Tewes, P., "Demonstration of Paragon's Ionomer-membrane Water Processing (IWP) Technology as a Purification Step for Lunar Water Processing," *50th International Conference on Environmental Systems*, July 2021, ICES-2021-295.
- ¹²Holquist, J.B., Pasadilla, P., Bower, C., Cognata, T., Tewes, P., and Kelsey, L., "Analysis of a Cold Trap as a Purification Step for Lunar Water Processing," *49th International Conference on Environmental Systems*, July 2020, ICES-2020-71.
- ¹³Holquist, J.B., Joyce, C.J., Rivera, R., Tewes, P., Myles, T., et al., "Demonstration of Paragon's ISRU Propellant Production Subsystem Electrolyzer and Electrolysis Assembly," *52nd International Conference on Environmental Systems*, July 2023, ICES-2023-108.

¹⁴Joyce, C.J., Holquist, J.B., Ruble, A., Rivera, R., and Moeller, T., “Demonstration and Model Validation of Freeze Distillation as a Purification Step for Lunar Water Processing,” *52nd International Conference on Environmental Systems*, July 2023, ICES-2023-136.

¹⁵Hurley, D.M., Gladstone, G.R., Stern, S.A., et al., “Modeling of the vapor release from the LCROSS impact: observations from LAMP,” *Journal of Geophysical Research*, Vol. 117, E00H07, 2012.

¹⁶Hurley, D.M., Siegler, M.A., Cahill, J.T.S., Colaprete, A., et al., “Surface Volatiles on the Moon,” *Reviews in Mineralogy and Geochemistry*, Vol. 89, No. 1, 2023, pp. 787-827.

¹⁷Bessone, J., “The activation of aluminum by mercury ions in non-aggressive media,” *Corrosion Science*, Vol. 48, No. 12, 2006, pp. 4243-4256.

¹⁸Pawel, S.J., DeSetfano, J.R., Mannes Schmidt, E.T., “Corrosion of Type 316L Stainless Steel in a Mercury Thermal Convection Loop,” *Oak Ridge National Laboratory*, 1999.

¹⁹Nichols, D.E., Nguyen, D.T., and Boles, J.L., “Corrosion of mild steel exposed to urea-ammonium sulfate suspensions,” *National Fertilizer and Environmental Research Center*, 1981.

²⁰Lobnig, R.E., Siconolfi, D.J., Maisano, J., et al., “Atmospheric corrosion of aluminum in the presence of ammonium sulfate particles,” *Journal of the Electrochemical Society*, Vol. 143, No. 4, 1996.

²¹Guo, Y., Liu, Z., Huang, Z., Liu, Q., and Guo, S., “Reaction Behavior of Sulfur Dioxide with Ammonia,” *Industrial & Engineering Chemistry Research*, Vol. 44, No. 26, 2005, pp. 9989-9995. Ref 14 and 18 from trade study TM

²²Kocsis, T., Magyari, J., Sajó, I., Pasinszki, T., “Evidence of quasi-intermolecular redox reactions during thermal decomposition of ammonium hydroxodisulphiteferriate(III),” *Journal of Thermal Analysis and Calorimetry*, Vol. 132, 2018, pp. 493-502.