Comparison of Four Strong Acids on the Precipitation Potential of Gypsum in Brines during Distillation of Pretreated, Augmented Urine

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Abstract

In this study, three different mineral acids were substituted for sulfuric acid (H_2SO_4) in the urine stabilizer solution to eliminate the excess of sulfate ions in pretreated urine and assess the impact on maximum water recovery to avoid precipitation of minerals during distillation. The study evaluated replacing 98% sulfuric acid with 85% phosphoric acid (H_3PO_4), 37% hydrochloric acid (HCl), or 70% nitric acid (HNO_3). The effect of lowering the oxidizer concentration in the pretreatment formulation also was studied. This paper summarizes the test results, defines candidate formulations for further study, and specifies the injection masses required to stabilize urine and minimize the risk of mineral precipitation during distillation. In the first test with a brine ersatz acidified with different acids, the solubility of calcium in gypsum saturated solutions was measured. The solubility of gypsum was doubled in the brines acidified with the alternative acids compared to sulfuric acid. In a second series of tests, the alternative acid pretreatment concentrations were effective at preventing precipitation of gypsum and other minerals up to 85% water recovery from 95th-percentile pretreated, augmented urine. Based on test results, phosphoric acid is recommended as the safest alternative to sulfuric acid. It also is recommended that the injected mass concentration of chromium trioxide solution be reduced by 75% to minimize liquid resupply mass by about 50%, reduce toxicity of brines, and reduce the concentration of organic acids in distillate. The new stabilizer solution formulations and required doses to stabilize urine and prevent precipitation of minerals up to 85% water recovery are given. The formulations in this study were tested on a limited number of artificially augmented urine batches collected from employees at the Johnson Space Center (JSC). This study successfully demonstrated that the desired physical and chemical stability of pretreated urine and brines can be achieved using alternate pretreatment formulations under laboratory conditions. Additional testing and hazard assessments will be required to determine the feasibility of utilizing the proposed urine pretreatment formulations on ISS.

1. INTRODUCTION

The Urine Processor Assembly (UPA) was introduced on the International Space Station (ISS) in 2008 in order to recover potable water from urine and reduce the required resupply mass of water. In October 2009, on-orbit operation of the UPA at 85% water recovery of pretreated urine caused precipitates that were identified as gypsum ($CaSO_4 \cdot 2H_2O$). The precipitates blocked pitot tubes within the Distillation Assembly (DA) and flooded the DA with brine that led to failure of the UPA. The gypsum precipitates, which were not observed in extensive ground testing, were attributed to both elevated in-flight levels of urinary calcium and sulfate ions and excess sulfate from the sulfuric acid (H_2SO_4) in the pretreatment formulation. The Russian pretreatment formulation, used in the Russian-provided waste collection system, uses sulfuric acid and hexavalent chromium as an oxidizer in the form of chromium trioxide (CrO_3). The UPA currently operates at 70% water recovery to minimize the precipitation potential in the DA. At 70% water recovery, only 62% of the urine mass is recovered as water from nominally pretreated urine.

Initial testing compared three strong acids to sulfuric acid in the pretreatment stabilizer solution formulation. The solubility of calcium in brines pretreated with the three acids was measured and compared to the baseline sulfuric acid formulation. The success criterion was full solubility of all organics and minerals at 85% water recovery from 95^{th}-percentile Pretreated Augmented Urine ($PTAU_{95}$) with nominal pretreatment dosing of about 88 doses per EDV-y (pretreated urine storage container on ISS) The testing was conducted utilizing an estimated 95^{th}-percentile calcium concentration of 0.26 g dissolved calcium per liter of raw urine based on analysis of wastewater sampled from nine returned Recycle Filter Tank Assemblies (RFTAs) (Gazda, 2010).

This work focused on measuring the chemical and physical properties of pretreated urine and brines and assessing the relationship between the pretreatment chemicals and the precipitation potential of minerals during distillation and storage.

The goal of this research was to maximize the mass of water that can be extracted from urine by distillation processors in microgravity. The overall objective of this series of tests was to optimize the pretreatment formulation to maximize water recovery without mineral precipitation while minimizing the required mass of pretreatment chemicals to stabilize urine for storage. The test variables were the type of acid, the concentration of the acid, and the concentration of the oxidizer.

Specific objectives were as follows:

- Quantify the ability of alternative strong acids to minimize the common ion effect and increase the solubility of calcium and minerals in brines.
- Optimize the oxidizer dosing concentration to prevent uric acid precipitation and improve distillate water quality while minimizing consumables and hazard levels.

- Using data from the first two objectives, define the required pretreatment formulation and dose that stabilizes urine and minimizes precipitation risks during distillation.

2. EXPERIMENTAL METHODS

2.1 SELECTED ACIDS TO REPLACE SULFURIC ACID

The three strong acids used as substitutes for sulfuric acid are listed in Table 1.

Table 1: Acids Used in Testing

Acid, Purity	Advantages	Disadvantages
Sulfuric, 98%	Keeps surfaces clean, decades of flight experience, very low vapor pressure	Excessive sulfate decreases calcium solubility in brines, has high reactivity
Hydrochloric, 37%	Increased calcium sulfate solubility	Fuming, corrosive, not compatible with hexavalent chromium
Nitric, 70%	Increased calcium sulfate solubility	Unstable when exposed to air and light, corrosive, forms ammonium nitrate salts
Phosphoric, 85%	Increased calcium sulfate solubility, low toxicity, provides buffering at pH 2	Weak acid, large dose required to reach pH = 2, decreased solubility of phosphates

2.2 PREPARATION OF HEXAVALENT CHROMIUM OXIDIZER SOLUTION

In addition to the mineral acids, an oxidizer solution was prepared, as part of the stabilizer solution that is added to urine. The oxidizer concentration (0.015 M in pretreated urine) currently used on ISS was used as a baseline stabilizer. The oxidizer solution was prepared by adding 165 g of CrO_3 to 1,000 g of Deionized (DI) water, using the safety procedures and preparation methods described in EC3-WR-088, Standard Operating Procedure for the Formulation of Batch Russian Pretreated Urine. The resulting solution had a mass density of 1.17 g/mL. A 0.004 M CrO_3 solution was also tested. For the reduced oxidizer dose, 41 g of CrO_3 were added to 1,000 g of DI water. The mass density of the reduced oxidizer solution was 1.04 g/mL. The reduced oxidizer dose was found to be effective at stabilizing urine by Putnam (1971).

2.3 EXPERIMENTS

Two types of experiments were conducted to compare the effectiveness of alternative pretreatment formulations to stabilize urine and prevent precipitation of gypsum during distillation. In the first test, the solubility of gypsum was measured in brine ersatz at a range of acid doses (pH values). In the second test, augmented human urine was pretreated with the alternate acids to provide the same pH as the baseline pretreatment dose. The pretreated urine was distilled to 85% water recovery. The brines were stored for 1 week and analyzed to measure the solubility of calcium and the mass concentration of suspended solids (precipitates).

Table 2: Summary of Tests to Evaluate Alternative Pretreatment Formulations

Test	Solution
Test 1	85% brine ersatz
Test 2	85% brine distilled from acidified and oxidized $PTAU_{95}$

2.3.1 Test 1: Solubility of Gypsum in Brine Ersatz

In Test 1, saturated solutions of gypsum were prepared by adding an excess of gypsum crystals to the solution of interest. The ersatz solutions represented brines with urinary organic and inorganic compounds. The solution was stirred for 7 days to reach chemical and physical equilibrium. The saturated solution was filtered using glass fiber filters (0.7 micron pore size), and the filtrate was analyzed by ion chromatography for total dissolved calcium and sulfate concentrations.

For this sequence of tests, on-orbit urine was simulated with a urine ersatz formulation developed by Verostko (2010), which has a theoretical ionic calcium concentration of 260 mg/L, equal to the maximum urinary calcium concentration expected in-flight. As a comparison, the mean urinary calcium concentration in-flight is about 188 mg/L. The ersatz formulation also contains 22.5 g of urea/L of urine. The concentration of major solutes in the 95th-percentile urine ersatz and augmented urine are listed in Table 3.

Table 3: Theoretical Concentrations of Major Solutes in 95th-Percentile Urine Ersatz and Augmented Urine

	Cl^- (mg/L)	Total PO_4 (mg/L)	Total SO_4 (mg/L)	Na^+ (mg/L)	Total Ammonia Nitrogen (TAN) (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Total Organic Carbon (TOC) (mg/L)
Urine Ersatz Formulation	5600	2300	3000	3000	590	2000	260	84	8500
Augmented Urine: 95th percentile	No target	3100	3000	No target	No target	No target	260	No target	9200

2.3.2. Test 2: Distillation of Pretreated, Augmented Human Urine

Urine was collected from volunteers at the Johnson Space Center (JSC). Urine was combined into batches, made up of 20% first morning void and 80% normal urine output. Each batch of urine also corresponded to a 5:1 male:female donor ratio.

The calcium ion concentration was measured in the raw urine prior to adding the augmentation chemicals. Once the calcium concentration was measured, inorganic and organic chemicals were added to reach 260 mg of Ca/L of raw urine, to represent a worst case scenario with respect to calcium precipitation. Other chemicals were added, in a linearly proportional amount, to the calcium addition, as described by Adam et al. (2010).

The augmented urine was pretreated and distilled under pressure and temperature conditions simulating nominal operation of the DA on ISS. The solutions used in initial testing represent the worst-case (most concentrated) in-flight urine solute concentrations. The maximum calcium concentration was assumed to be 260 mg of Ca/L of raw urine, based upon a statistical analysis of in-flight urinary data. After stabilization chemicals and flush water are added, the calcium concentration is reduced to 206 mg of Ca/L of pretreated urine.

The theoretical mixture of urine, flush water, and stabilizer solution are given in Table 4. Previous ground testing at JSC and MSFC used the values in Table 4 to pretreat urine prior to 2010. The values in Table 5 are an updated recipe of flushed urine based on RFTAs returned from ISS (Gazda, 2010). The values in Table 5 represent the concentration of stabilization agent and flush water used for all testing in this report. The theoretical concentration of total chromium is 0.8 g-Cr/L of pretreated urine solution (0.015 M) using the baseline pretreatment on ISS shown in Table 5. DI water was used to represent the Waste and Hygiene Compartment (WHC) flush water.

Table 4: Baseline Pretreated Urine Formulation
(used in ground testing at MSFC and JSC prior to 2010)

Constituent	Volume
Raw urine	1 L
Deionized (flush) water	0.25 L
Stabilizer solution	16.7 mL
Pretreated urine solution	1.267 L

Table 5: Pretreated Urine Formulation Based on Returned RFTAs (Gazda, 2010)

Constituent	Volume
Raw urine	1 L
Deionized (flush) water	0.265 L
Stabilizer solution	15.9 mL
Pretreated urine solution	1.281 L

Prior to distillation, the pretreated urine was stored at least 1 day at ambient temperature (20 – 25 °C) to allow the solution to approach an equilibrium state for the slow oxidation-reduction processes. The time between pretreatment and distillation was recorded, as the effect of storage time on precipitation potential during distillation is unknown.

A rotary evaporator (Rotavapor®, Buchi model R-215) was used to distill the pretreated urine. The initial mass of the pretreated urine to be distilled was measured in the glass evaporation flask on a 3 kg scale. The mass was recorded to the nearest 0.1 gram. The initial mass of pretreated urine ranged from 300 to 500 g. The evaporation flask was connected to the stop cock and vapor duct of the rotary evaporator.

The pretreated urine was distilled under vacuum to simulate nominal DA conditions. The absolute pressure within the evaporation flask was maintained at 60 to 80 mbar and the associated vapor temperature was measured as 39 to 41 °C. The evaporation vessel rotated at 45 rpm half-submerged in a heating bath, which was filled with tap water. The heating bath temperature was controlled at 60 ± 5 °C nominal. The chiller liquid temperature was set to 10 to 15 °C. Distillate condensed on glass surfaces in the condenser and drained by gravity into the distillate collection flask. The percent recovery was calculated by measuring the mass of brine solution at the end of a distillation run and comparing it to the initial mass of pretreated urine.

Following distillation to reach the targeted water recovery rate of 85%, the pressure and temperature were brought to ambient and the mass of the evaporation flask was measured; this allowed the mass of remaining brine to be determined, followed by the exact water recovery rate. The brine was stored in the evaporation flask for one week at 25 °C to allow solid-liquid phase equilibrium by providing sufficient time for crystal formation if the brine was supersaturated with respect to a mineral.

Following 1 week of storage, the mass of brine was re-measured and the mass density of the brine was measured with a hydrometer or in a volumetric flask on a scale. A measured mass of brine was passed through a 0.7 micron glass fiber filter to measure Total Suspended Solids (TSS), Fixed Suspended Solids (FSS), and Volatile Suspended Solids (VSS) and to isolate any crystals. The evaporation flask and the solids on the filter were rinsed thoroughly to collect any crystals that adhered to the flask's glass surfaces. All of the brine from the evaporation flask was passed through the filter paper. If the quantity of suspended solids was significant, more than one filter paper was used.

The soluble concentration of calcium and the mass quantity of precipitates in distilled brines were the key parameters monitored in order to determine the reliability and effectiveness of the alternate acid formulations. The main precipitate of interest for the given pretreatment chemicals was gypsum; other precipitates of interest were phosphates and uric acid.

The masses of precipitates were monitored by measuring TSS and FSS retained on a glass fiber filter with an average pore size of 0.7 microns (0.6 to 0.8 microns nominal). The pretreated urine and brine were analyzed for TSS, FSS, and VSS. Measuring FSS and VSS enabled quantification of organic and inorganic suspended solids.

3. Results and Discussion

3.1 TEST 1

The solubility of gypsum in brines with both inorganic and organic constituents is shown in Figure 1. Solubility of calcium acidified with the three alternative acids increases with decreasing pH, whereas it decreases with the baseline sulfuric acid pretreatment due to the common ion effect. The overall effect of the alternative acids compared to sulfuric acid was a doubling in the solubility of gypsum in the ersatz brine (representing 84% water recovery). Hence, there is no advantage to adding more sulfuric acid to try to dissolve more calcium. Although a pH of 3 has the highest calcium solubility for the baseline formulation with H_2SO_4, this pH was found to be ineffective against a mold challenge in pretreated urine in a separate test. No oxidizer was used in this test.

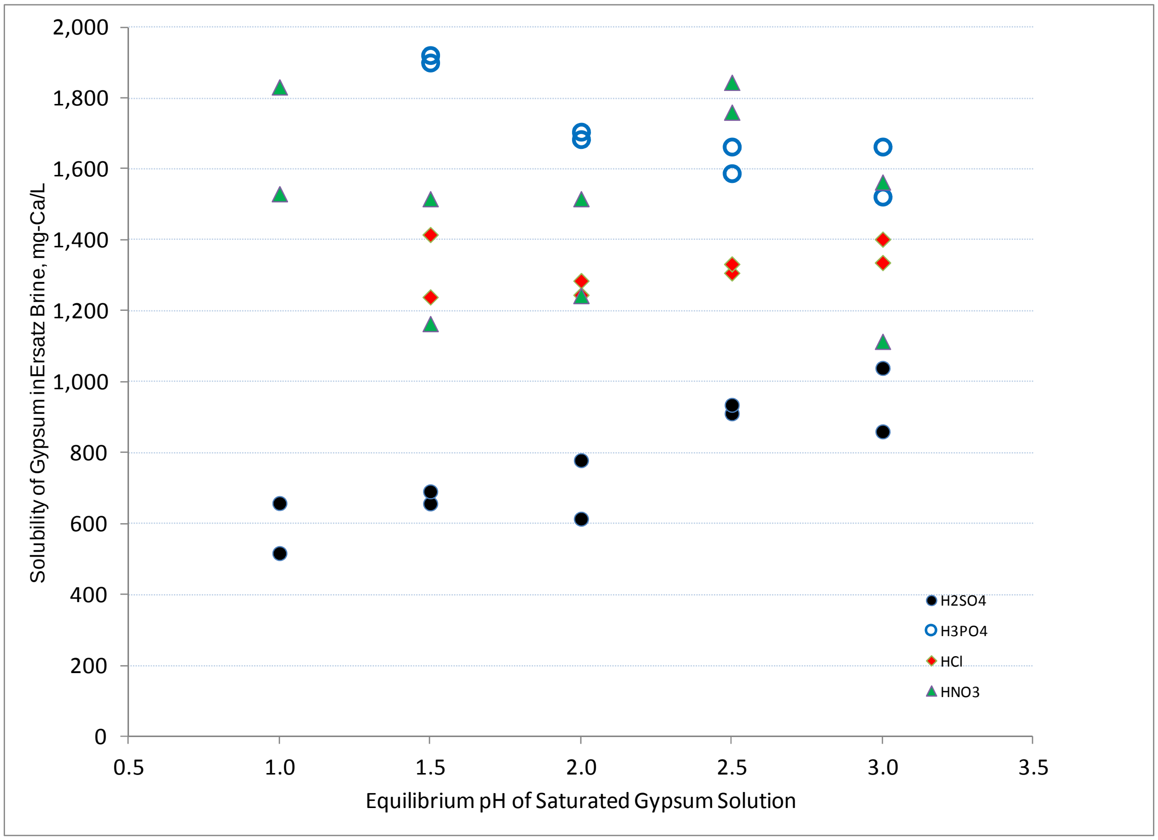

Figure 1: Solubility of Gypsum in Inorganic-Organic Brine Ersatz

3.2 TEST 2

Testing with the ersatz brine in Test 1 confirmed that the alternative acids were effective at increasing the solubility of gypsum (calcium sulfates) in ersatz brine solutions compared to the baseline acid (sulfuric acid) by a factor of about two. Test 1 was conducted by equilibrating artificial urine brine solutions with an excess of gypsum crystals and measuring the amount of calcium that would dissolve. The next step was to evaluate the more realistic processes of gypsum solubility in brines during the distillation of real urine solutions with calcium concentrations representing the upper 95th percentile ($PTAU_{95}$).

Experiments were conducted to evaluate the effectiveness of the alternative acids at preventing precipitation of minerals during distillation of real urine. The question to be answered was if the alternative acids would permit distillation of $PTAU_{95}$ to 85% recovery without precipitation of minerals. The effect of three different oxidizer (hexavalent chromium) concentrations were measured: (1) no oxidizer, (2) the reduced oxidizer dose (0.002 M), and (3) the baseline oxidizer dose (0.015 M) in pretreated urine. The main parameter used to monitor the quantity of mineral precipitates was the mass concentration of FSS. In addition, the mass concentration of VSS was measured to quantify the precipitation of uric acid, a poorly soluble organic compound found in urine. The goal was to determine the type of acid (H_2SO_4, H_3PO_4, HCl, and HNO_3), the required alternate acid doses to reach the equivalent pH of the baseline pretreatment formulation using sulfuric acid (pH 2), and the oxidizer concentration (0.0 M, 0.002 M, and 0.0015 M) that minimized both inorganic and organic precipitates (TSS) in 85% recovery brines.

Figures 2 and 3 show the effect of pretreatment formulations on TSS in real brines.

Figure 2 shows the mass concentration of FSS and VSS in brines that were distilled to 85% recovery from $PTAU_{95}$ that was acidified but not oxidized.

Without an oxidizer, uric acid precipitates at 1 to 2 g/kg of brine for all acids, including the baseline sulfuric acid. The formation of uric acid crystals in acidified urine brines is a slow process compared to the formation of gypsum crystals. The induction time is on the order of 1 week for uric acid crystals to form from supersaturated urine solutions. Uric acid is poorly soluble and will precipitate in pretreated urine even without distillation. In this study, uric acid crystals were identified based on their amber color and morphology.

Figure 3 shows that the alternative acids prevent mineral precipitation up to 85% water recovery. The error bars represent ± one standard deviation for triplicate distillations of $PTAU_{95}$. FSS values are less than 30 mg/kg of brine for all three alternative acids compared to an average FSS of 1.9 g/kg for the baseline sulfuric acid. The VSS values are less than 125 mg/kg of brine for all three alternative acids and 320 (reduced oxidizer dose) to 580 mg/kg (full oxidizer dose) for the sulfuric acid brine.

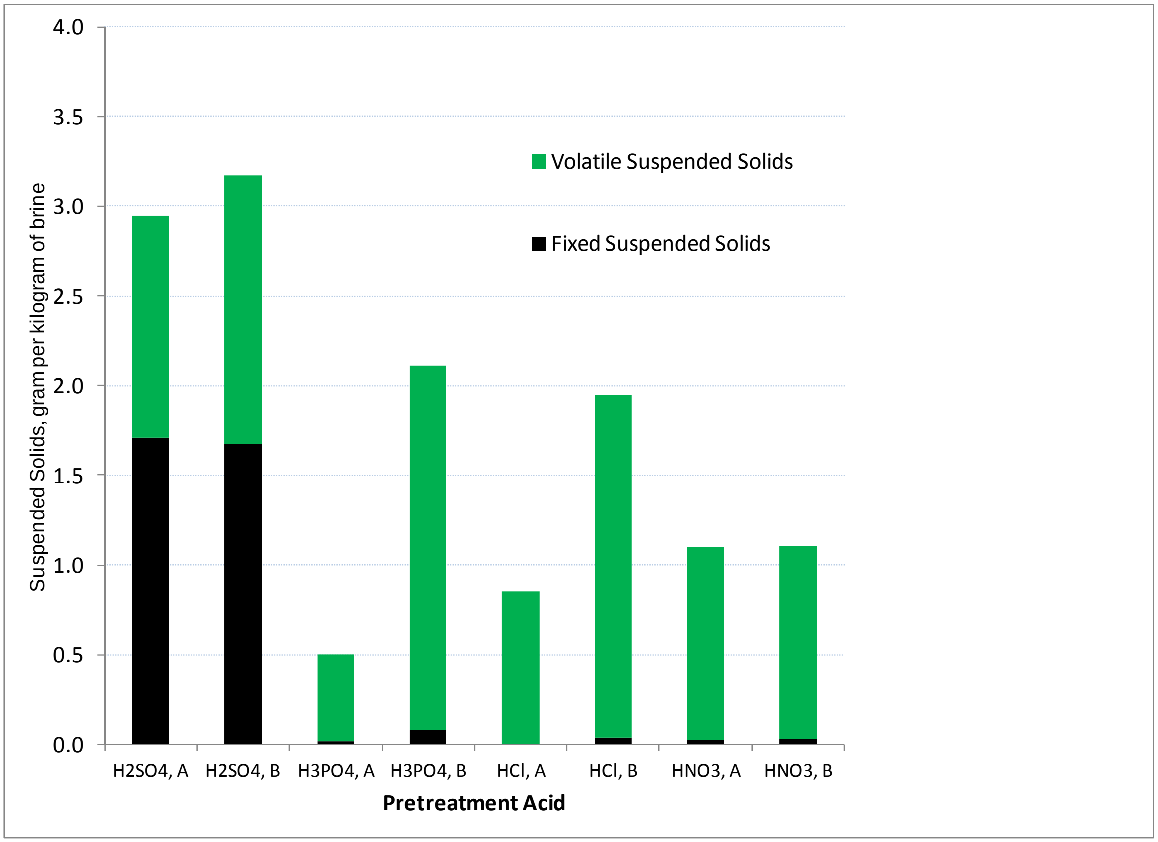

Figure 2: Suspended Solids in 85% Brines Without Oxidizer

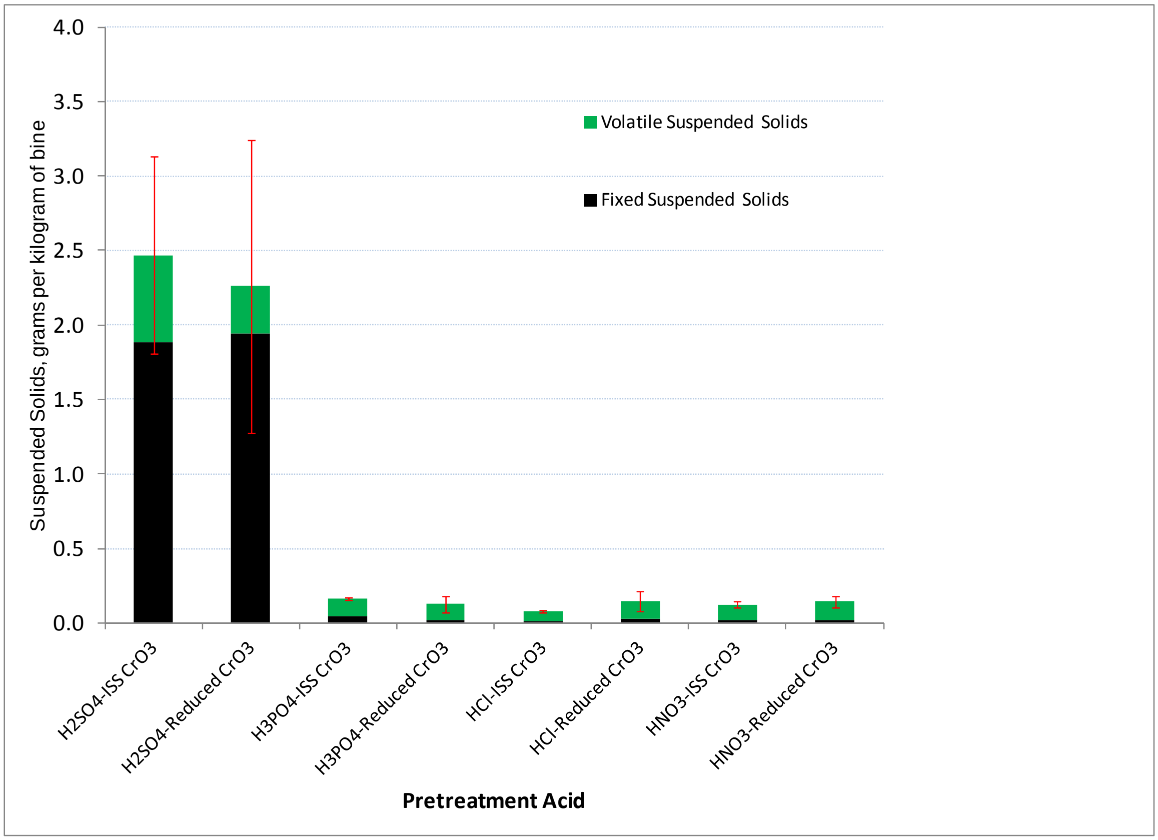

Figure 3: Suspended Solids in 85% Brines With Oxidizer

The concentration of dissolved calcium ions was measured for all the filtered brines after being stored for 1 week. All of the alternative acid brines at 85% recovery had dissolved concentrations of about 1,400 mg-Ca/L compared to 700 mg-Ca/L for the baseline pretreatment brine with sulfuric acid.

4 Recommended Formulations

The new formulations would utilize the same hardware that is currently used on ISS. The current pretreatment formulation is launched and transported in a 5-L tank that links to the pretreatment/water dispenser pump of the Russian toilet in the WHC. The new formulations prepared with phosphoric acid or nitric acid would use the same 5-L tank. In the case of hydrochloric acid, two separate tanks would be required because concentrated hydrochloric acid is not compatible with oxidizer. The relative compositions of the formulations are listed in Table 6. Dosing requirements to achieve equivalent pH values as the current baseline pretreatment are given in Tables 7 through 10.

Similar to the current pretreatment formulation using sulfuric acid, the new formulations combine a concentrated acid with an aqueous solution of hexavalent chromium. Proper Personal Protective Equipment (PPE) and safe laboratory practices in a fume hood are required to prepare and store these solutions.

One liter of the new pretreatment solution using phosphoric acid is prepared by dissolving 24.3 g of CrO_3 in 147 mL of DI water. Next, 853 mL of 85% phosphoric acid are added to the 147 mL of chromium solution to make 1 L of stabilizer. The pretreatment solution is 89.4% concentrated phosphoric acid (includes water contained in concentrated phosphoric acid), 9.1% water (used to dissolve CrO_3), and 1.5% chromium trioxide by mass. Five liters of this solution are required to fill the pretreatment tank on ISS. Five liters of solution are sufficient to stabilize 254 L of raw urine.

One liter of the new pretreatment solution using nitric acid is prepared by dissolving 47 g of CrO_3 in 284 mL of DI water. Next, 716 mL of 70% nitric acid are added to the 284 mL of chromium solution to make 1 L of pretreatment solution. The pretreatment solution is 73.4% concentrated nitric acid (includes water contained in concentrated nitric acid), 21.2% water, and 3.5 % chromium trioxide by mass. Five liters of this solution are required to fill the pretreatment tank on ISS and will stabilize 490 liters of raw urine. Due to the hazardous nature of nitric acid and its potential decomposition into oxides of nitrogen when exposed to air, the nitric acid formulation would be more hazardous than the current formulation utilizing sulfuric acid.

Table 6: Relative Mass Content of Stabilizer Solutions in 5-Liter Tank Prior to Pretreatment of Urine

	Mass Density of Stabilizer Solution at 20 °C	**Concentrated Acid Solution**	**Water to Dissolve CrO_3**	**CrO_3**
Baseline stabilizer solution with 98% H_2SO_4	1.35 g/mL	36.5%	54.5%	9.0%
Alternative stabilizer solution with 85% H_3PO_4	1.62 g/mL	89.4%	9.1%	1.5%
Alternative stabilizer solution with 70% HNO_3	1.35 g/mL	75.4%	21.1%	3.5%
Alternative stabilizer solutions with 37% HCl	1.20 g/mL	100%	0%	0%
	1.17 g/mL	0%	85.8%	14.2%

Note: *Percentages by mass. The formulation with HCl would require two separate tanks (one for the acid and one for the oxidizer solution).*

Due to oxidation of chloride ions by chromic acid, hydrochloric acid is not compatible with the oxidizer solution at the tested concentrations; the oxidizer solution and concentrated acid would have to be added separately to the urine if hydrochloric acid were to replace sulfuric acid. The high vapor pressure and corrosiveness of 37% hydrochloric acid would also be problematic for flight applications.

Long-term stability of the alternative stabilizer solutions during storage and materials compatibility were not included in this testing.

Table 7: Volume and Mass of Stabilizer Solutions To Be Injected in Each Dose With Flush Water

Nominal Doses per Liter of Raw Urine Based on 9 Returned RFTAs	Acid	mL-Stabilizer Solution per Dose (1 injection)	mL-Flush Water per Dose (1 injection)
5.3	98% H_2SO_4 (current baseline operations on ISS)	3.0	50
5.3	85% H_3PO_4	3.7	50
5.3	70% HNO_3	1.9	50
5.3	37% HCl	2.5	50

Table 8: Concentrations of Stabilizer Chemicals Relative to Raw Urine for Nominal Dosing

Acid	g-Pure Acid per kg of Raw Urine	g-Cr per kg of Raw Urine
98% H_2SO_4 (current baseline operations on ISS)	7.7 g-H_2SO_4/kg	1.0 g-Cr/kg
85% H_3PO_4	24.2 g-H_3PO_4/kg	0.25 g-Cr/kg
70% HNO_3	7.2 g-HNO_3/kg	0.25 g-Cr/kg
37% HCl	5.9 g-HCl/kg	0.25 g-Cr/kg

Table 9: Concentrations of Stabilizer Solution Volumes and Masses Relative to Raw Urine for Nominal Dosing

Acid	g-Stabilizer Solution per kg of Raw Urine	mL-Stabilizer Solution per kg of Raw Urine
98% H_2SO_4 (current baseline operations on ISS)	21.5 g /kg	15.9 mL/kg
85% H_3PO_4	31.8 g/kg	19.6 mL/kg
70% HNO_3	13.6 g/kg	10.1 mL/kg
37% HCl	15.9 g/kg	13.3 mL/kg

The values listed in Tables 8 and 9 are based on obtaining a pH of 2 in the pretreated 95th-percentile urine. If the requirement can be increased to a pH greater than 2 in the future by additional testing, the mass of stabilizer solutions could be reduced. This would require brine precipitation testing and a long-term bacteria and mold challenge test at a pretreated urine pH of about 2.2 to 2.3.

Table 10: Concentrations of Stabilizer Chemicals in Flushed, Pretreated Urine (PTU) for Nominal Dosing

Acid	g-Pure Acid per kg of PTU	g-Cr per kg of PTU
98% H_2SO_4 (current baseline operations on ISS)	6.0 g-H_2SO_4/kg-PTU	0.78 g-Cr/kg-PTU
85% H_3PO_4	18.6 g-H_3PO_4/kg-PTU	0.19 g-Cr/kg-PTU
70% HNO_3	5.6 g-HNO_3/kg-PTU	0.19 g-Cr/kg-PTU
37% HCl	4.6 g-HCl/kg-PTU	0.19 g-Cr/kg-PTU

5. Summary and Conclusions

Three different strong acids were substituted for sulfuric acid in the urine pretreatment formulation. These alternative acids eliminated the excess of sulfate ions coming from sulfuric acid that reduce the solubility of calcium in brines. The concentrated acids studied were 85% phosphoric, 37% hydrochloric, and 70% nitric acid. The effect of lowering the oxidizer concentration also was studied in order to save consumable mass and improve distillate water quality. This paper summarized the test results and defined the new formulations and the injection masses required to stabilize urine. The tested pretreatment concentrations were effective at preventing precipitation of gypsum and other minerals up to 85% water recovery from $PTAU_{95}$.

Phosphoric acid is recommended as the safest alternative acid to replace sulfuric acid. It also is recommended that the injected mass concentration of chromium trioxide solution be reduced by 75% to minimize resupply mass and reduce elevations in brine pH associated with oxidation processes.

By enabling UPA operations at 85% water recovery instead of the current 70%, the new formulation with phosphoric acid would permit recovery of an additional 193 g of water per kg of raw urine compared to the pretreatment formulation currently used on ISS. For a crew of three astronauts on ISS for 1 year, this equates to 274 kg of additional water from urine. The new formulation also would reduce the mass of brine produced by the UPA by 193 g/kg of raw urine processed, corresponding to a reduction of 274 kg of hazardous brine per year for a crew of three. The required mass of pretreatment solution will increase from 21.5 g/kg of raw urine to 31.9 g/kg for the phosphoric acid formulation. This corresponds to an annual liquid mass increase from 30.6 kg of the current sulfuric acid pretreatment to 45.4 kg of the new phosphoric acid solution for a crew of three.

Implementation of the pretreatment would not require major hardware changes. The new urine stabilizer solution could be launched, stored, and delivered in the 5-L pretreatment tank that is currently used for the sulfuric acid pretreatment solution on ISS. Volumes of 3.7 mL of pretreatment solution and 50 mL of flush water would be injected in one dose by the pretreat/water dispenser pump upstream of the fan separator in the Russian toilet (compared to the current 3.0 mL baseline injection dose). Five liters (8.1 kg) of the new solution are sufficient to stabilize 254 L of raw urine (65 day supply for a crew of three). As a comparison, 5 L (6.8 kg) of the prior urine pretreatment solution with sulfuric acid were sufficient to stabilize 315 kg of raw urine (81 day supply).

Future testing with a 3.0 mL injection of the phosphoric acid formulation are planned to determine if it is sufficient to stabilize urine and prevent mineral precipitation in brines.

The formulations and data in this document were tested on a limited number of artificially augmented urine batches collected from employees at JSC. This work demonstrated the desired physical and chemical stability of pretreated urine under laboratory conditions. Additional testing will be required to determine the feasibility of utilizing the proposed pretreatment formulations on ISS. Continued collection of statistical data on in-flight urinary concentrations of calcium, sulfate, and phosphate would be helpful in assessing the precipitation potential of any given pretreatment formulation.

To summarize, the main conclusions for each alternative acid were:

A. Based on experimental results and practical considerations, phosphoric acid is the safest alternative acid of the three tested to replace sulfuric acid.
B. The formulation with nitric acid was also effective at preventing mineral precipitation in 85% brines and stabilizing urine with a low resupply mass

requirement, but concentrated nitric acid is considered to be more hazardous and less stable than phosphoric acid. Ammonium nitrate salts also present safety issues if brines were distilled to dryness.

C. Hydrochloric acid was effective at preventing precipitation in 85% brines and stabilizing urine with a very low resupply mass requirement , but it reacts with hexavalent chromium, so it would have to be stored and injected separately from the oxidizer solution. Concentrated hydrochloric acid also has a high vapor pressure and is corrosive.

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