

Ion Exchange Technology Development in Support of the Urine Processor Assembly Precipitation Prevention Project for the International Space Station

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In support of the Urine Processor Assembly Precipitation Prevention Project (UPA PPP), multiple technologies were explored to prevent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) precipitation during the on-orbit distillation process. Gypsum precipitation currently limits the water recovery rate onboard the International Space Station (ISS) to 70% versus the planned 85% target water recovery rate. Due to its ability to remove calcium cations in pretreated augmented urine (PTAU), ion exchange was selected as one of the technologies for further development by the PPP team. A total of 13 ion exchange resins were evaluated in various equilibrium and dynamic column tests with solutions of dissolved gypsum, urine ersatz, PTAU, and PTAU brine at 85% water recovery. While initial evaluations indicated that the Purolite SST60 resin had the highest calcium capacity in PTAU (0.30 meq/mL average), later tests showed that the Dowex G26 and Amberlite FPC12H resins had the highest capacity (0.5 meq/mL average). Testing at the Marshall Spaceflight Center (MSFC) integrates the ion exchange technology with a UPA ground article under flight-like pulsed flow conditions with PTAU. To date, no gypsum precipitation has taken place in any of the initial evaluations.

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I. INTRODUCTION

The urine processor assembly (UPA) on the International Space Station (ISS) recovers water from urine via a vacuum distillation process. The distillation occurs in a rotating distillation assembly (DA) where the urine is heated and subjected to sub ambient pressure¹. As water is removed, the original organics, salts, and minerals in the urine become more concentrated and result in urine brine. Eventually, water removal will concentrate the urine brine to super saturation of individual constituents and precipitation occurs. Under typical UPA DA operating conditions, calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or gypsum is the first chemical to precipitate in substantial quantity. Under nominal urine conditions, the UPA can achieve 85% water recovery without precipitation. However, on ISS it is possible that urine calcium can be significantly elevated for some individuals. As previously described¹, the gypsum has precipitated in the DA when operating at water recovery rates at or near 85% and caused the failure of the DA and required its replacement. Subsequent investigation has demonstrated an excess of both calcium and sulfate, the precipitation occurs at water recovery rates greater than 70%. The source of the excess calcium is physiological in nature, via crewmembers' bone loss, while the excess sulfate is primarily due to the sulfuric acid component of the urine pretreatment. To prevent gypsum precipitation in the UPA, the Precipitation Prevention Project (PPP) team has focused on removing the calcium ion (Ca^{2+}) from pretreated urine. While a number of technologies have been tested for this purpose, the focus of this report is on ion exchange resins as calcium removal agents. Thirteen resins were selected for evaluation in both equilibrium flask and dynamic column testing. This report outlines the work completed in support of down-selecting these resins to one that can be used for flight.

The specific objectives for ion exchange resin evaluations include:

- Identify the resin(s) with the highest calcium ion capacity and quantify its calcium capacity under flight-like conditions.
- Determine the sensitivity to flow rate through a resin column for optimum calcium removal under flight-like conditions.
- Determine the volume of resin needed to support on-orbit operations based on ground test data.

II. MATERIALS AND METHODS

Ion exchange is a reversible ion interchange between a solid material and a liquid in which there is no permanent change in the structure of the solid. Commercial ion exchange resins consist of a spherical polymer matrix with specific chemical functional groups on their surface. The selectivity and effectiveness of ion exchange resins are determined by factors such as the mobility of the liquid phase through the polymer matrix, the density of functional groups, type of functional groups bound to the matrix, and the chemical characteristics of the liquid phase (pH, oxidation potential, and ionic strength). Depending on their polymer structures, resins are typically classified as macroporous (large pores) or gel-type (small pores), and strong/weak acid or strong/weak base depending on the type of functional group. Resins were selected based on a review of manufacture literature and discussions with NASA, industry, and academic experts. A summary of resins tests for the UPA PPP technology evaluation is listed in Table 1 below. The minimum capacity refers to manufacture data for calcium uptake in a dilute aqueous neutral pH solution. All tests were conducted in the JSC Water Analysis Laboratory unless noted otherwise.

Table 1. Summary of ion exchange resins and their chemical properties.

Company	Dow						Purolite			Rohm & Haas			Biorad
Name	G-26	50WX4-400	M4195	MAC3	Marathon C	50WX4-800	SST104	SST60	S940	FPC12-H	FPC22-H	IRC747	Chelex 100
Ionic Form	H+	H+	BP	Na+	Na+	H+	H+	Na+	Na+	H+	H+	Na+	CA

Func'l Group*	SA	SA	CH	CA	SA	SA	CA	SA	AP	SA	SA	AP	CH
Matrix [†]	S-DVB	S-DVB	S-DVB	P-DVB	S-DVB	S-DVB	P-DVB	P-DVB	S-EB	PS	PS	S-DVB	S-DVB
Min. Capacity (meq/mL)	3	1.1	1.21	3.8	2	1.1	3.8	4.56	1	1.35	1.7	1.75	0.4

*SA= sulphonic acid, CA= carboxylic acid, CH= chelating, AP= aminophosphonic groups, IM= imino-diacetic acid, BP= bis-picolylamine. [†]S-DVB= styrene-divinylbenzene, P-DVB= polystyrene-divinylbenzene, S-EB= styrene-ethenylbenzene, PS= polystyrene

A. Equilibrium Testing

To down-select to a specific resin, a series of tests was performed to evaluate each resin's calcium capacity with a variety of solutions. Solution volumes varied from 0.5 to 1 L and were held in Erlenmeyer flasks. Each resin test consisted of five flasks with a fixed liquid volume and varying quantities of resin. The mass of calcium in solution was always in excess of the total calcium removal capacity for each quantity of resin. The difference between the initial calcium concentration and after the resin reach equilibrium represented the maximum calcium the resin could remove in the ion exchange process. Flasks were capped and stirred overnight, with samples taken after approximately 24 hours. Chemical analysis was performed as described in the Analytical Methodology section. Up to five different fluids were used in the equilibrium testing with each resin. The test fluid preparation is briefly described here and a more detailed description will be released in a future NASA technical memorandum.

Gypsum Solution Equilibrium Testing

Initial equilibrium evaluations were performed to determine the maximum calcium capacity of the resins in varying quantities when exposed to a deionized water solution containing 1.2g/L gypsum. These tests determine the maximum possible amount of calcium that can be removed by each resin under the "ideal" (neutral pH and no oxidizers or competing ions) conditions described above.

Six (6) g of gypsum were dissolved in 5 L of deionized (DI) water. Five different quantities of a particular resin were placed in 1-L flasks, and 990 mL of the gypsum solution added to each flask. The remaining 50 mL of solution served as the control sample.

Urine Ersatz Equilibrium Testing

After completion of the gypsum-only evaluations, tests with a urine ersatz solution were performed to determine the interference effect of other ions on the resin calcium removal capacity. Resins that are subject to a high degree of interference in the ersatz, and hence a highly diminished calcium capacity, were removed from the test matrix. The chelating resin, Dowex M4195, is designed to operate at a low pH and was therefore not evaluated in this stage of the test series.

Ersatz test solutions were prepared using a concentrated stock and additional CaSO₄, per EC3-WR-088, *Collection, Augmentation, Stabilization, and Disposal of Urine*. No chemical pretreatments were added. The target concentrations for each major ion in the urine ersatz working solution are shown in Table 2.

Table 2. Major ion concentrations in urine ersatz working solution.

	Cl ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TOC
Concentration (mg/L)	5569	2347	3009	2971	13202	2000	280	84	8456

Pretreated Urine Ersatz Equilibrium (PTE) Testing

Four resins were tested with PTE, including the three down-selected resins and the Dowex M4195. The PTE was made using the ratio of 1 L ersatz working solution (defined above): 0.25 L DI water flush:16.7 mL pretreatment/stabilizer solution. The stabilizer solution was identical to the on-orbit ISS stabilizer and consisted of 90 g CrO₃ in 545 mL DI water, with 365 g concentrated H₂SO₄ added to that mixture.

Pretreated Augmented Urine (PTAU) Equilibrium Testing

A limited number of tests with PTAU₉₅ were conducted. PTAU₉₅ consisted of collected human urine with the same pretreatment dosing and flush water addition as the urine ersatz solution. The collected urine was pooled to achieve a 1:5 ratio of first morning void-to-daytime void and a 1:6 male-to-female ratio. In addition to these ratios, the urine was augmented with specific compounds to reach a targeted calcium concentration of 260 mg/L in the urine, or 205 mg/L in the working solution.² This represents the 95th-percentile calcium concentration measured in samples obtained from 9 Recycle Filter Tank Assemblies (RFTAs) returned from ISS.

B. Dynamic Column Testing

The initial dynamic column test involved pumping 20 L of pretreated microgravity urine ersatz through an ion exchange column. The three down-selected resins from pretreatment testing were evaluated in a 100-mL packed column as shown in Figure 1. The column was 1.25 in (3.175 cm) in diameter, with an internal length: diameter ratio (L/D) of 4:1. The column was a packed bed configuration with a compression spring providing a preload to prevent fluidization and channeling. The column was tested vertically with flow entering from the bottom.

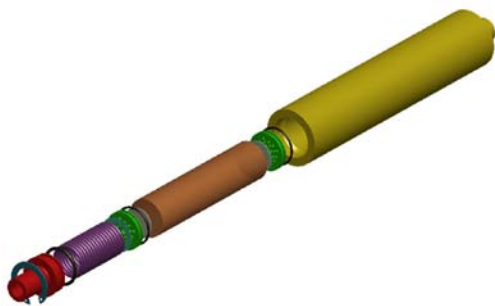


Figure 1. Ion exchange column.

Figure 2 shows the layout for ion exchange flow-through testing. A 20-L carboy was used to hold the initial batch of pretreated urine ersatz solution. The solution was pumped through the packed column at a flow rate of 100 mL/min (6 L/hr), with testing at other flow rates shown in Table 3. Test durations ranged from approximately 3-9 hours. The dynamic column tests were run until resin exhaustion. Exhaustion is the point at which the resin is saturated with respect to calcium and the calcium concentration in the effluent is equivalent to the influent (no calcium uptake); the exhaustion point was verified analytically. The test matrix was based on a resin capacity of 1 meq/mL, a bed/column size of 100 mL, and

a working Ca²⁺ concentration of approximately 205 mg/L. Pressures and flow rates were logged on an hourly basis at a minimum. Chemical samples for each test were taken as described in the Analytical Methodology section of this document. Later flow-through tests evaluated the two highest-performing resins with PTAU, using the same test paradigm as the PTE.¹

Several locations within and upstream of the UPA were possible locations to implement ion exchange columns. There is limited pressure drop tolerance within the UPA so a wide range of flow rates were tested to evaluate a wide range of specific velocity conditions and its effect on adsorption capacity.

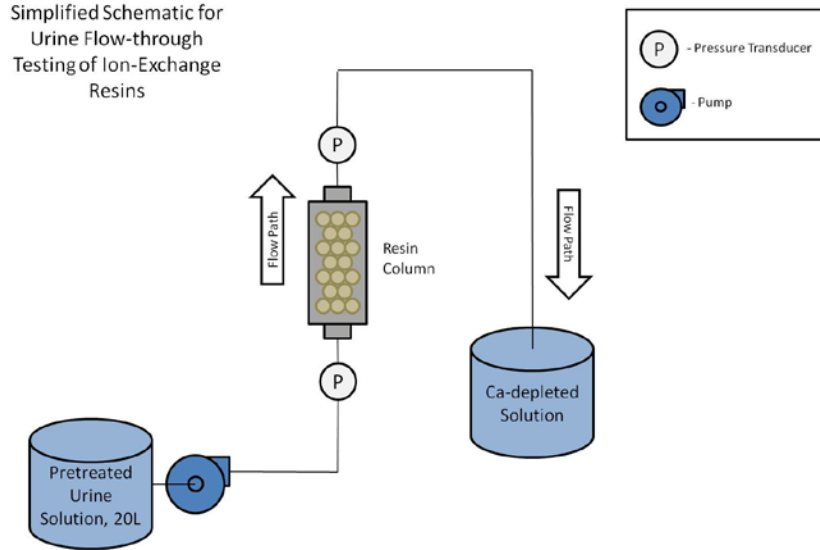


Figure 2. Schematic of augmented urine flow-through testing of ion-exchange resins.

Table 3. Ion exchange resin flow-through test matrix.

Flow Rate			Ca ²⁺ Flow Rate	Batch Volume	Test Duration
(L/Hr)	(mL/min)	(lb/Hr)	(meq/Hr)	(L)	(Hr)
3	50.00	6.61	16.58	19.91	6.64
6	100.00	13.23	33.15	19.91	3.32
0.5	8.33	1.10	2.77	19.89	39.78

C. Analytical Methodology

Equilibrium Testing Analytical Methodology

Forty (40)-mL samples were collected from the control solution at the beginning of each test and from each flask after the completion of a test run. For both the control and test samples, pH and ion concentrations were measured. Ion analyses were performed using ion chromatography (IC). IC data was used to calculate the resin capacity for each resin using the following formula:

$$Ca \text{ Capacity of Resin} = \frac{(C_o - C_f) \times (V_{\text{solution}}) \times \left(\frac{2 \text{ meq}}{\text{mmol}} Ca\right) \times \rho_{\text{resin}}}{M_{\text{resin}} \times \left(\frac{40.08 \text{ mg}}{\text{mmol}} Ca\right)}$$

where C_o and C_f are the initial (control) and final concentrations of Ca, respectively, in mg/L, ρ_{resin} is the density of the resin, V_{solution} is the volume of urine solution added to the resin, and M_{resin} is the mass of resin. The solution volume is in liters (L), and the mass of the resin is in grams (g). The Ca capacity of each resin was calculated in units of meq Ca per mL resin (equal to eq/L). Each equilibrium test consisted of five flasks with five different quantities of resin and the capacity of each flask's resin was determined separately. The average of those five values was used when comparing the various resins.

Dynamic Column Tests Analytical Methodology

Forty (40)-mL samples were collected at regular intervals throughout each column test. As the calcium adsorption capacity of the resin in the column was depleted, the amount of Ca^{2+} in the effluent increased. Eventually, the effluent Ca^{2+} concentration plateaued, indicating resin exhaustion. Because the timescale to reach resin breakthrough is initially unknown, samples were taken at equally spaced intervals (of 30 minutes or less) in an effort to generate a breakthrough plot similar to Figure 3. Time was manually recorded with a stop watch and volume through-put was based on the average pump flow rate. The area under the curve was integrated to determine the total calcium adsorption capacity. A steeper breakthrough curve is normally desired because it presents a more efficient use of the resin. However, in order to prevent precipitation in the UPA, only 50% of the influent calcium must be removed from the influent. As a result, calcium capacity is most important, with resin efficiency as a secondary goal.

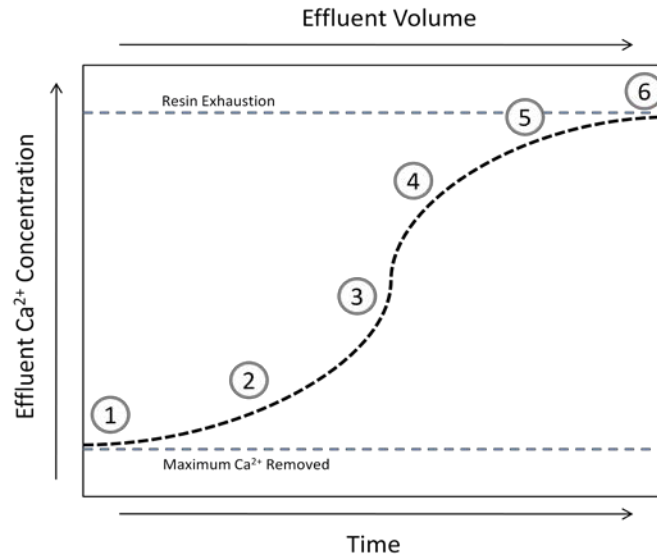


Figure 3. Typical calcium concentration versus time and volume for the effluent during dynamic ion exchange column testing. Sample points are numbered 1-6.

III. RESULTS AND DISCUSSION

A. Equilibrium Testing

Gypsum Test Results

Calcium capacities as a function of concentration ratio are shown in Figure 3. These values represent the “best-case” performance for each resin, as described in section II-A above. This testing shows that each resin performs similarly regardless of initial calcium concentration; the various initial calcium concentrations are shown as individual data points for each resin in Figure 3. Ion exchange resins with the highest calcium capacities were noted and tested with the PTE ersatz formulation.

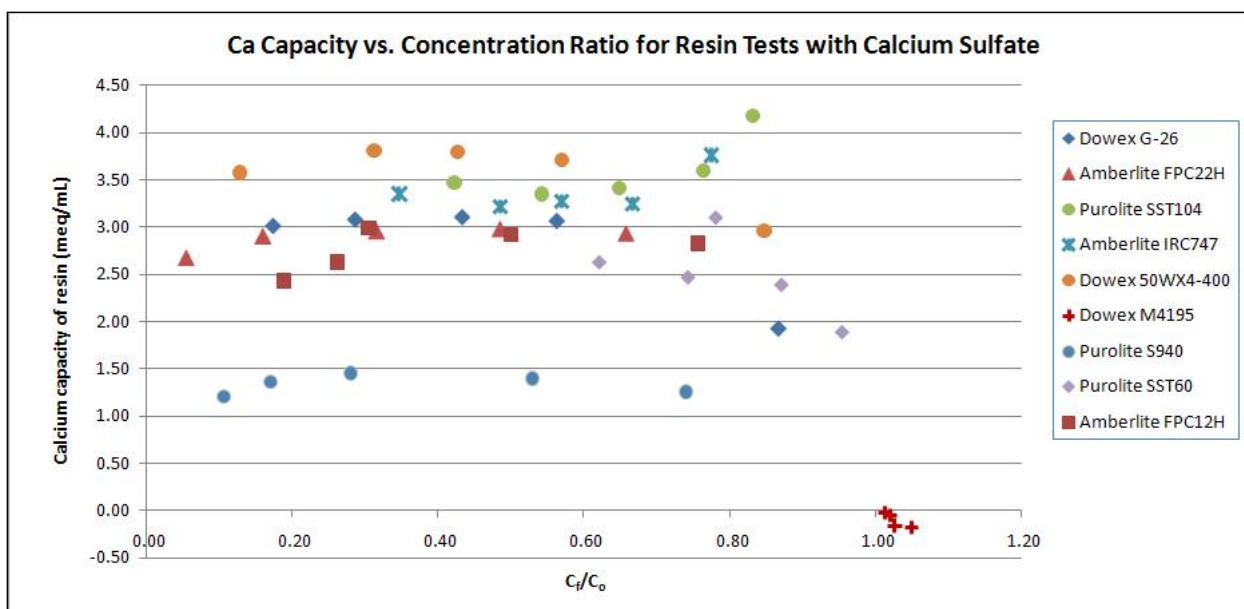


Figure 4. Calcium capacity versus concentration ratio for gypsum evaluations.

Urine Ersatz and Pretreated Urine Ersatz (PTE) Results

Microgravity urine ersatz equilibrium testing was performed per the method described in section II-C. The three ion exchange resins with the highest calcium capacities were the Purolite SST60, Purolite SST104, and the Amberlite IRC747. These top performing resins were evaluated with the pretreated ersatz formulation. In addition to these resins, the Dowex M4195, MAC3, Marathon C, and 50WX800 resins were tested in PTE. Little to no calcium removal was seen with the Marathon C, M4195, or the IRC747.

Pretreated Augmented Urine (PTAU) Results

Two resins from the PTE equilibrium evaluations were tested with PTAU: SST60 and MAC3. An additional abbreviated (three data point) equilibrium test of the SST104 and Chelex 100 resins was conducted with PTAU. A summary of test results for all of the equilibrium evaluations is shown in Figure 4.

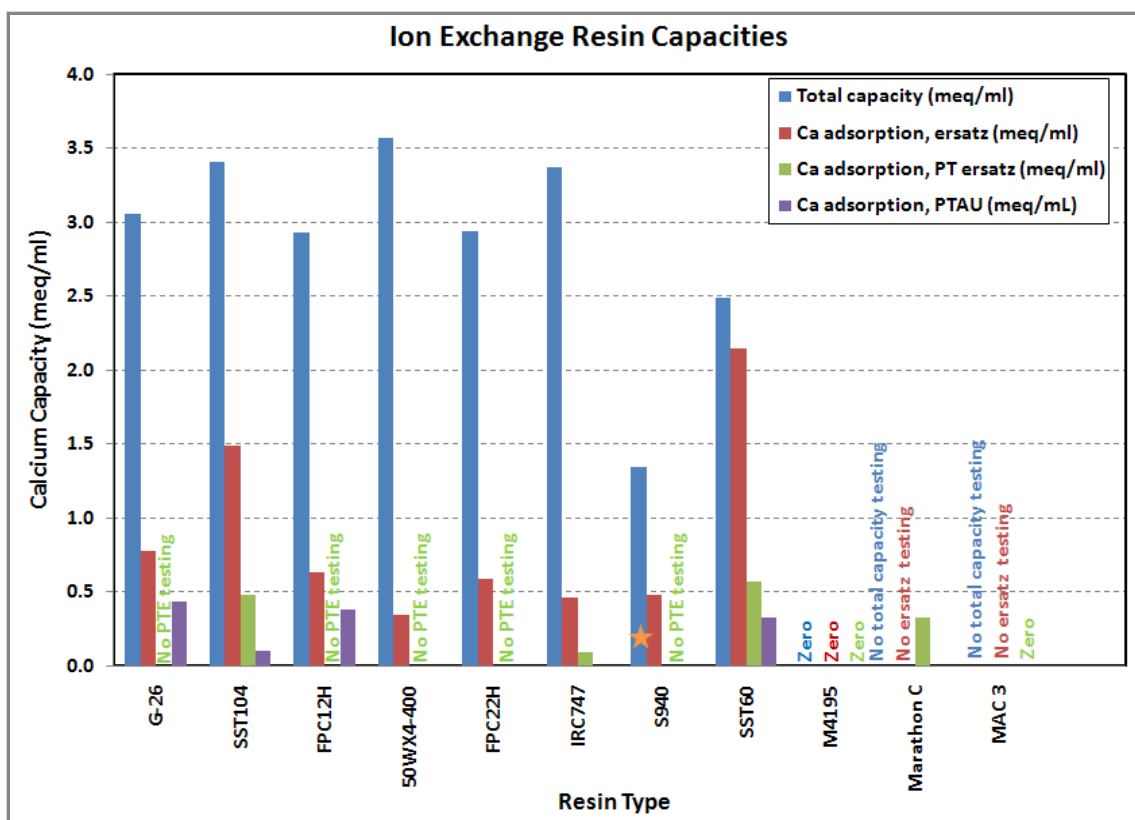


Figure 1. Summary of ion exchange equilibrium test results.

Early dynamic column tests with SST60, SST104, and MAC3 resins displayed significant variability in performance from one replicate to the next. To minimize the statistical variation in individual data points, a “multi-resin” equilibrium test was conducted to compare front-runner and previous resin candidates in PTAU. While less individual replicates were used, a higher mass of resin was present in each replicate, with each resin tested simultaneously with the same batch of PTAU. This mitigated batch-to-batch variability in PTAU and performance variations on the resin bead level. Fixed quantities of resin—3 g and 6 g—were equilibrium tested for the following five resins: SST60, SST104, MAC3, G26, and FPC12H. The capacities for each resin and mass are shown in Table 4 below. Due to the relatively high calcium capacities demonstrated by the Dowex G26 and Amberlite FPC12H resins in PTAU, they were selected for further evaluation in later column tests. The results of the multi-resin test resulted in not continuing of column tests with the SST60, SST104, and MAC3 resins and switching to primarily Dowex G26 because it was the best performing resin.

Table 4. Ion uptake data for multi-resin equilibrium test.

Date	Sample	Na (mg/L)	NH4 (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Vol Resin (mL)	Ca Capacity (meq/mL)	Average Ca Capacity (meq/mL)
3/4/11	PTAU feed	1909	219	1485	193	<0.5			
3/8/11	SST60 3g	2115	208	1363	193	<0.5	2.5	0	0.34
3/8/11	SST60 6g	2393	206	1302	126	<0.5	5	0.67	
3/8/11	SST104 3g	2207	209	1415	186	<0.5	2.5	0.14	0.10
3/8/11	SST104 6g	2549	204	1405	187	<0.5	5	0.06	
3/8/11	MAC3 3g	1872	209	1438	191	<0.5	2.5	0.04	-0.01
3/8/11	MAC3 6g	1869	207	1396	199	<0.5	5	-0.06	

3/8/11	G26 3g	1798	205	1357	149	<0.5	2.5	0.88	0.86
3/8/11	G26 6g	1727	199	1264	110	<0.5	5	0.83	
3/8/11	FPC12 3g	1804	207	1381	151	<0.5	2.5	0.84	0.76
3/8/11	FPC12 6g	1830	209	1344	125	<0.5	5	0.68	

B. Dynamic Column Testing

Pretreated Ersatz Results

Early PTE testing indicated that the Purolite SST60 had the highest equilibrium capacity. Although SST60 was later replaced with G26 as the leading candidate, the performance of SST60 under varying conditions is insightful to overall resin performance in the challenging UPA conditions. The SST60 resin was subjected to dynamic column testing at flow rates of 6, 0.5, and 3 L per hour (Lph). The Purolite SST104 was also tested at 6 Lph and 3 Lph to compare its performance to the SST60. Finally, the Dowex MAC3 was tested at 3 Lph.

The effluent cation concentrations correlate with the expected competition between ions for available functional groups in the ion exchange resin. The three primary factors that govern ion exchange resin uptake are charge, size, and concentration. Because of their relatively low charge, monovalent cations are generally outcompeted by divalent cations; that is, a divalent calcium or magnesium will “bump” (outcompete) a monovalent like sodium or potassium off the resin. While the expectation is that chromium (either trivalent or hexavalent) will outcompete calcium due to charge, size and concentration advantages, that is not observed in dynamic column testing. The mechanism by which the calcium outcompetes the chromium is not fully understood. However, it should be noted that the chromium/sulfuric acid pretreatment does impact the *total* resin capacity, which may provide some insight into why the calcium is not outcompeted during the test. If that is the case, then the other cations would be left to compete for any remaining functional groups between each other, in proportion to their charges/sizes/concentrations.

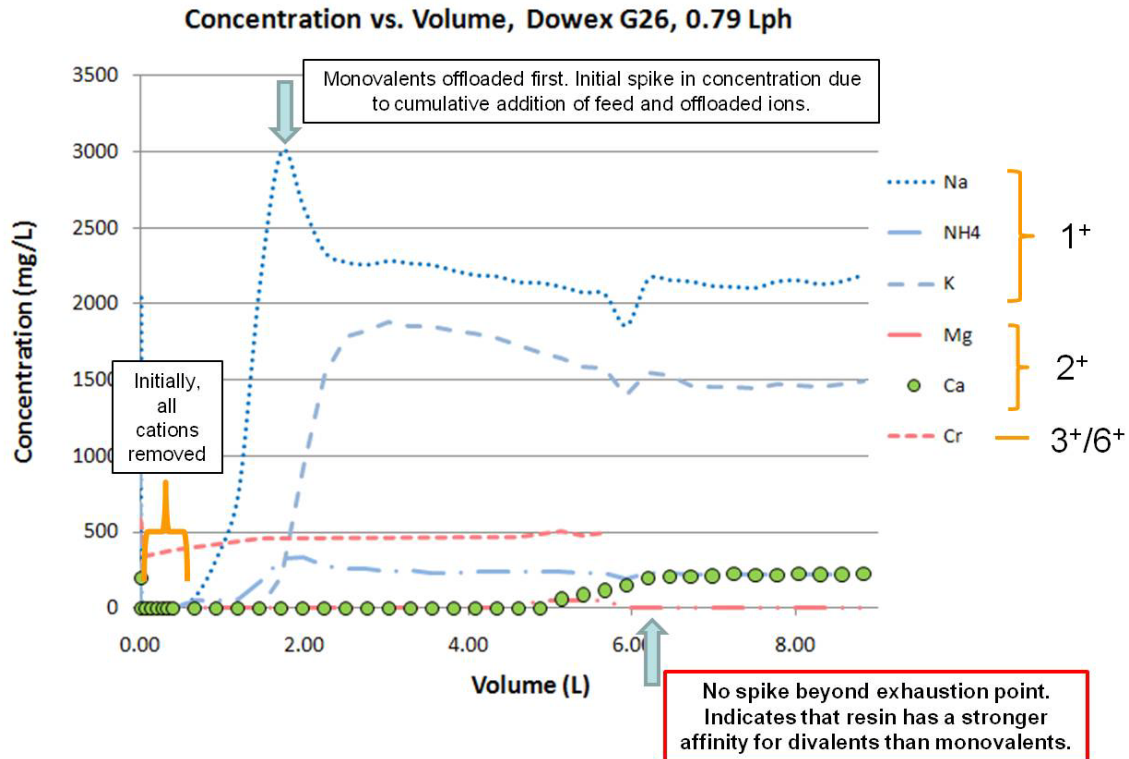


Figure 2. The factors between affinity for various ions by an ion exchange resin.

To further characterize the calcium capacity as a function of flow rate, dynamic column tests were conducted at a flow rate of 3 Lph with the SST60, SST104 and MAC3 resins. Because the SST60 and SST104 resins did not reach complete exhaustion by the end of testing, their breakthrough curves were extrapolated using a linear curve fit to the estimated exhaustion point. The resulting extrapolated equilibrium capacities for each resin are 0.294 meq/mL for SST60, 0.273 meq/mL for SST104, and no uptake for the MAC3.

Pretreated Augmented Urine Results

Of the potential on-orbit locations for an ion exchange column was downstream of the Wastewater Storage Tank. Preliminary sizing of the column for acceptable pressure drop required a superficial velocity (SV) of 1 meter per hour (mph). This equates to a volumetric flow rate of 0.79 Lph in the subscale ion exchange evaluation column. Figure 5 shows the results of a dynamic column test using the SST60 resin in PTAU at 0.79 Lph. A total of 4.12 L of PTAU was flowed through 115 mL of resin, and the resin was nearly exhausted by the end of the test. Extrapolation of the breakthrough curve resulted in a total calcium capacity of 0.31 meq/mL. This equates to a total of 721.4 mg of calcium removed from the test solution.

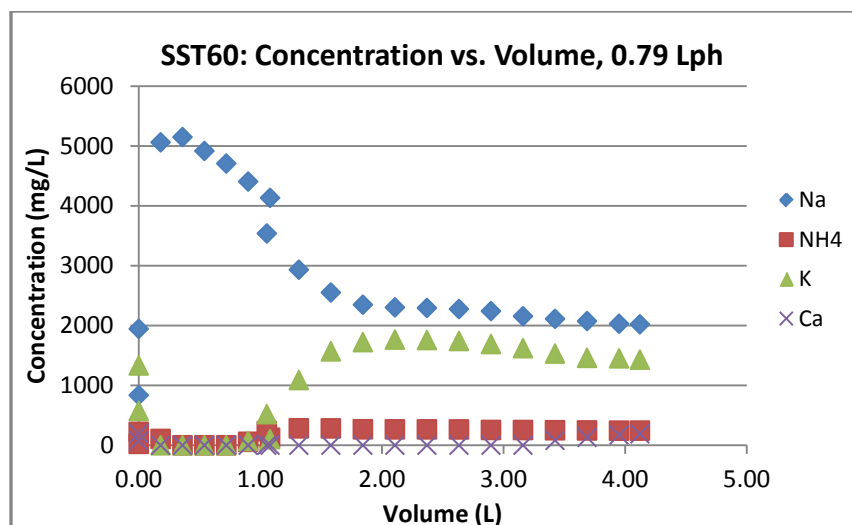


Figure 3. Concentration versus volume for the Purolite SST60 resin at a superficial velocity of 1 mph.

After the completion of this test, the multiple resin test (summarized in Table 4 above) was conducted, indicating that the Dowex G26 resin had a higher calcium capacity than the SST60 in PTAU. To verify the result of the multi-resin equilibrium test, a column test was conducted with the Dowex G26 at 1 mph SV; this test setup will hereafter be referred to as “Test 1.” For Test 1-1 (the first replicate), the resin did not reach exhaustion, so the column was further tested. The resulting calcium capacity of the G26 resin, including the calcium removal observed from the extended run on 3/24/11, was 0.497 meq/mL. This higher capacity confirmed that the G26 outperformed the SST60 when exposed to PTAU, even under flow conditions. In addition, no chromium removal was observed for the duration of the test.

After the initial Dowex G26 column test, it was selected by the PPP team at the April 5, 2011 Technical Interchange Meeting (TIM) for further pre-flight evaluations. A second test (Test 1-2) of the G26 at an L/D of 4 and volumetric flow rate of 0.79 Lph was conducted on. After Test 1-2, increased concern about pressure drop through an elongated column prompted an investigation into a departure from the traditional minimum L/D of 4 to 2.2. This was mechanically accomplished by adding a spacer to the subscale column, which retained the internal diameter but reduced the resin bed length by 2.96 in. Tests at an L/D of 2.2 and a volumetric flow rate of 0.79 Lph will hereafter be referred to as “Test 2.”

Tests 2-1, 2-2, and 2-3 were conducted to evaluate the impact of decreasing the L/D on the calcium capacity of the ion exchange resin. Capacities for the three replicates were 0.476, 0.233, and 0.461 meq/mL, respectively. The second replicate (Test 2-2) showed substantially reduced calcium uptake compared to other test runs. The influent calcium concentration was 142 mg/L, which is markedly lower than for other tests (which averaged 200.1 mg/L). It is theorized that the low calcium concentration may have negatively impacted its competition with other ions for the ion exchange functional groups.

Test 3 was developed by reevaluation of flow rates that would occur during on-orbit WHC-UPA usage resulted in slight changes to the test flow rate. An average crew of three would produce 18 voids a day (six per crewmember). Assuming an average urine void and pretreatment of 400 mL, this equates to a total daily volume of 7.2 L of urine produced each day. Including the assumption that urine voids occur over a 16 hour period on-orbit, the average daily volumetric flow rate for urine is 0.45 Lph. Test 3 was conducted with an L/D of 2.2 and a volumetric flow rate of 0.45 Lph. Using a linear curve fit for the breakthrough curve, calcium capacities for the Test 3 replicates were 0.523 and 0.440 meq/mL, respectively (see Figure 7 for Test 3-2 breakthrough curves).

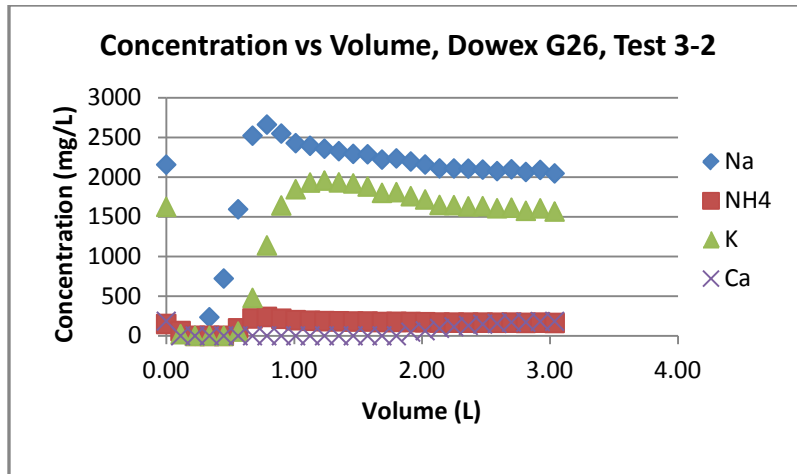


Figure 4. Concentration versus volume for the Dowex G26 resin under test 3 conditions.

Test 4 was required after further evaluation of potential on-orbit locations for an ion exchange column resulted in a change in implementation strategy. Instead of being placed downstream of the Waste Storage Tank Assembly, the column would be placed in line with the WHC Urine Jumper, upstream of the PTU T-Valve between the WHC and the UPA. This location has a higher SV (13.2 mph) than the previously-identified location but is more accessible by the crew and less sensitive to pressure drop. This particular location would be exposed to the pulsed flow of individual urination events; therefore, additional testing was conducted to simulate those events. Scaling from flight parameters to the subscale column was done using the SV of 13.2 mph, which equates to a subscale volumetric flow rate of 10.45 Lph. To average out to a flow rate of 0.45 Lph, each pulse would have to be 14 seconds long with a pulse occurring every 5.5 minutes (5.27 minutes from the end of one pulse to the beginning of the next). This test setup, which was conducted with the Dowex G26 resin at an L/D of 2.2, will be referred to as “Test 4.” Calcium capacities for each replicate were 0.409, 0.537, 0.540 meq/mL, respectively. The result for Test 4-1 is not included as a valid test point since it does not directly scale to a flight application. A summary of the test 1-4 results can be seen in Table 6.

Table 5. Summary of Dowex G26 column tests and calcium capacities.

Test Number	Resin Volume (mL)	L/D	Superficial Velocity (mph)	Volumetric Flow Rate (Lph)	Flow Pattern	Test Dates (2011)	Calcium Capacities (meq/mL)
1	115	4	1	0.79	Continuous	3/18, 5/9	0.497, 0.396
2	55	2.2	1	0.79	Continuous	5/6, 5/31, 6/23	0.476, 0.233, 0.461
3	55	2.2	0.57	0.45	Continuous	5/13, 6/22	0.523, 0.439
4	55	2.2	13.2 (during flow)	10.45 (during flow)	Pulsed	5/16, 6/24, 7/21	0.409, 0.537, 0.540

Because the influent concentrations for each test varied, it is undesirable to make a direct comparison between data sets from different tests. To make comparisons between calcium breakthrough curves, the effluent concentrations must be scaled to the influent concentrations, and volumetric flow rates must be scaled to number of bed volumes flowed through for each test. Figure 8 shows the calcium breakthrough curves for tests 1-4, where C/C_0 is the effluent sample concentration scaled to the influent concentration. The sodium, potassium, and ammonia ion break through still occur but are omitted for clarity. Breakthrough occurred at roughly the same number of bed volumes for all tests; the average breakthrough

bed volumes per test type for each cation can be seen in Figure 9. The high number of bed volumes for calcium shows the resin's strong preference for that cation, regardless of flow rate or L/D.

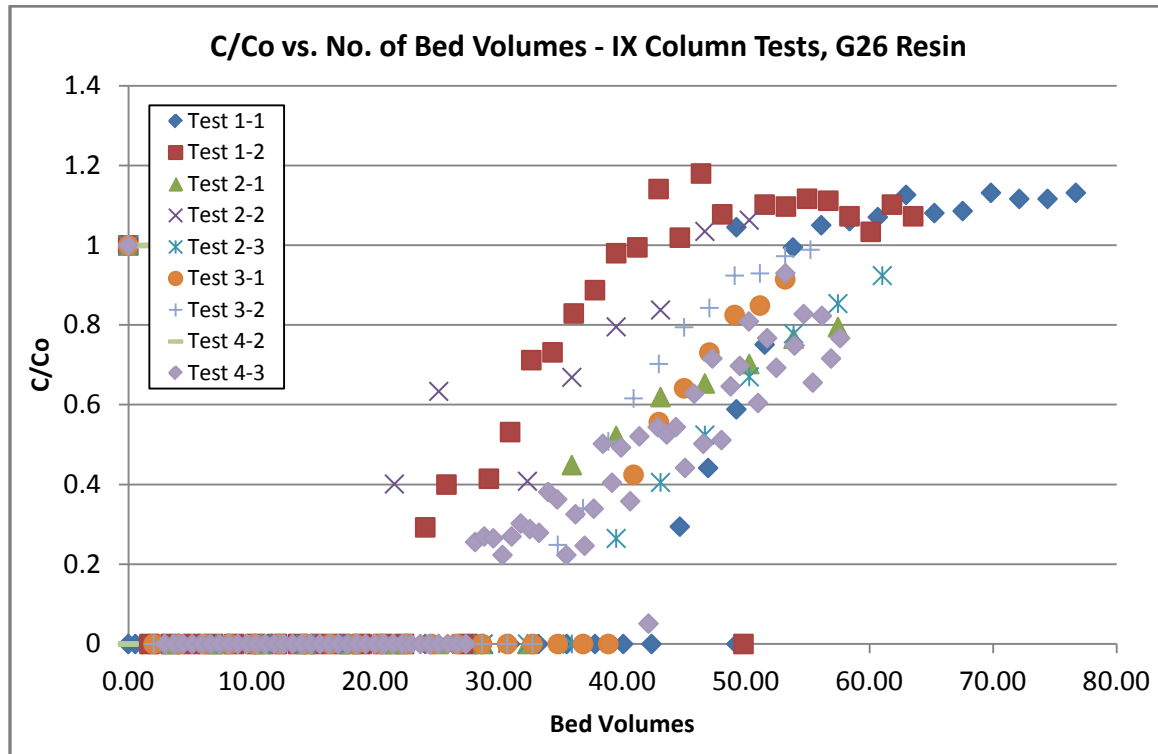


Figure 5. Scaled concentration versus scaled throughput for the Dowex G26 resin, tests 1-4.

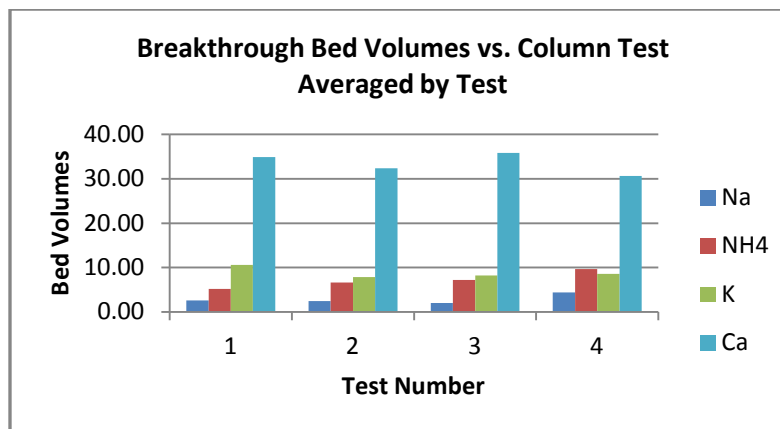


Figure 6. Number of bed volumes at which various cations reached breakthrough for the Dowex G26 resin, tests 1-4.

Additional tests were conducted, under Test 3 flow conditions, to determine the impact of variations in solution chemistry on calcium uptake by the resin. Solutions that were explored included both high and low pretreatment doses and low calcium concentration. Variations in pretreatment dosing were determined by looking at on-orbit data, using an average pretreatment dose of 5.3 dose pump injections per liter of raw urine. The range of dosing used for this test was 3.36 doses/L urine (5th percentile) and 7.84 doses/L urine (95th percentile).

Calcium concentrations for the low and high pretreatment doses were 170 and 128 mg/L, respectively. It should be noted that the low calcium concentration for the high pretreatment test was due to dilution effects from the increased dose volumes. The low calcium test concentration was 180 mg/L; while lower than the average for the rest of the “nominal” column tests, it was not as low as in the pretreatment evaluations. In addition, test 2-2 showed lower than expected calcium concentration (142 mg/L), so it offers another data point in determining the effect of calcium concentration on resin performance.

For both the low pretreatment and low calcium tests, the subscale resin column did not reach breakthrough, therefore a calcium capacity could not be calculated. However, the resin did remove more calcium than expected, which implies that lowering the pretreatment dose will improve resin performance. For the high pretreatment dose test, the resin did reach breakthrough, but did not reach exhaustion. Using a linear curve fit to the calcium breakthrough curve, the extrapolated calcium capacity was 0.369 meq/mL. This is a marked decrease from the average capacity seen for nominal pretreatment dose evaluations. While additional replicates of these tests should be performed, these initial results indicate that pretreatment dose levels and calcium capacities are inversely related.

Additionally, while the low-calcium test did not show decreased resin performance, the actual calcium concentration achieved in that solution was within 10% of the target concentration (with a 10% measurement accuracy); it is possible, therefore, that the concentration for that test was not low enough to cause a substantial change in calcium uptake by the resin. The two lowest-concentration tests (test 2-2 and the high-pretreatment dose test) had sharply reduced capacities as compared to other tests: 0.233 and 0.369 meq/mL, respectively. These two test points may indicate that lower calcium concentrations do negatively impact resin performance. The potential reasons for the impact are two-fold. First, the lower calcium concentration allows it to be out-competed by cations at higher concentrations. Second, the statistical likelihood of a calcium ion finding an available functional group on the resin surface is lower because there is a lower number of calcium ions in solution. The impact of low calcium concentration on resin performance is a potential limiting factor and should be further explored when designing an ion exchange column for flight.

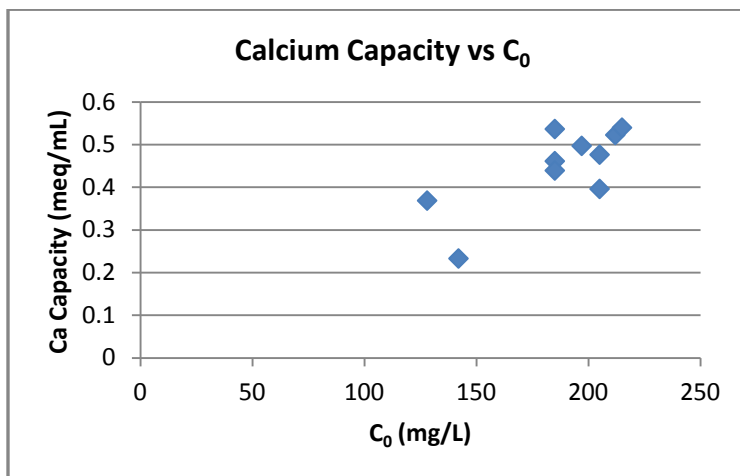


Figure 7. Calcium capacity as a function of influent calcium concentration for test condition #3. A general increase in capacity can be seen as C_0 increases.

Finally, an analysis of pH versus calcium capacity was conducted to see if low pH negatively impacted capacity. No significant trend could be distinguished; however, test 2-2 did have higher pH and a low capacity (see Figure 11). The change in capacity for that test is believed to be due to the low calcium concentration for that test, not the elevated pH. As was seen with unpretreated versus pretreated equilibrium evaluations, the resin has historically performed better in a neutral solution and without pretreatment.

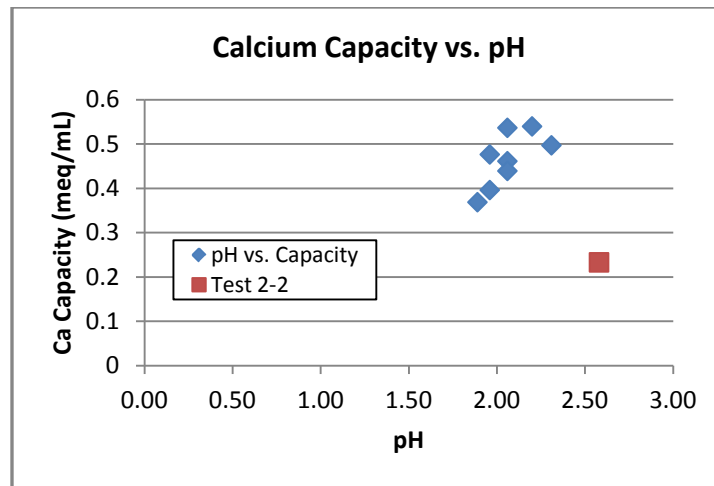


Figure 8. pH versus capacity for the Dowex G26 resin. While most capacities and pHs fall within a narrow range, Test 2-2 is an outlier in both pH and capacity.

Based on these subscale a larger scale column containing G26 resin was designed and tested in the ground UPA at MSFC. Those results will be discussed in a separate paper, but the larger scale performance has correlated well with the subscale results.

FPC12H Testing

The Amberlite FPC12H resin had the second-highest calcium capacity in the multi-resin test (0.76 meq/mL average) and was not initially selected after the multi-resin test. However, the ion exchange testing was extended to investigate alternate resins due to the earlier challenges identified in solely relying on equilibrium data. To further investigate the FPC12H resin's a column test was performed (under test 3 conditions) with the FPC12H and PTAU. Only a few initial tests have been performed to date. While the resin did reach breakthrough with respect to Na, NH₄, and K, it did not break through with respect to calcium. The Dowex G26 resin typically reached breakthrough at 1-2 L of flow-through volume, and reached exhaustion at 2-3 L flow-through. In contrast, 3.5 L of PTAU (at 196 mg/L calcium concentration) was flowed through the FPC12H column, and 100% of the calcium was removed for the duration of the test.

To confirm the results of the first column test, a replicate was performed, with an influent calcium concentration of 170 mg/L; again, 100% of the calcium was removed for the duration of the test. For each test, the quantities of calcium removed were 686.0 and 650.3 mg, respectively. For the G26 resin, an additional 130-180 mg of calcium was typically removed from breakthrough to exhaustion. Assuming a similar performance with the FPC12H (140 mg calcium removed from breakthrough to exhaustion) and that the resin would have shown breakthrough at the next data point, the calcium capacity is 0.718 meq/mL; this is a 50% increase in calcium capacity as compared to the G26 resin, and indicates that the volume of resin could be decreased by one-third by using the FPC12H rather than the G26. Further evaluation of the FPC12H resin to determine its calcium capacity is planned. Future testing will flow a much higher volume of PTAU through the column, increasing the chances of finding the breakthrough point of the resin.

Tracer Testing

Tracer testing was conducted using a subscale column, Dowex G26, and a dye (fluorescein) to determine if channeling was taking place in the ion exchange column. Channeling would inhibit the calcium uptake capability of the resin; therefore, channeling must be characterized and prevented as much as possible. As the name implies, fluorescein is a fluorescent yellow dye, most widely used in eye exams. Two-hundred (200) mL of a stock solution of 213.7 mg/L fluorescein was added to DI water to bring the total volume to 500 mL. The fluorescein was dissolved in the methanol solution first to prevent it from precipitating, since fluorescein powder is not soluble directly in DI water. To maximize the sensitivity of the test, all sample

absorbances were measured at the peak absorbance wavelength, 452.0 nm (Figure 13) with a Hach UV-Vis spectrometer.³

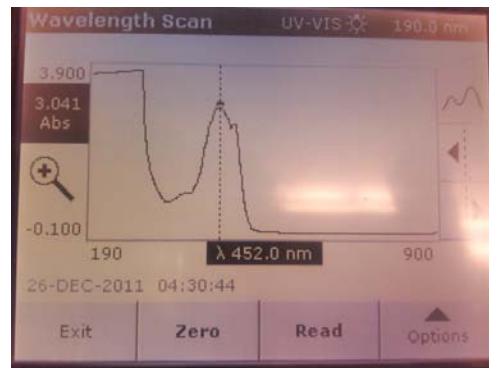


Figure 9. Wavelength scan of fluorescein solution.

A 150-mL slug of the fluorescein solution was pumped through a subscale column packed with 55 mL of Dowex G26 resin. Samples were taken every minute to characterize the change absorbance (and thereby solution concentration) over time. Figure 13 shows the absorbance concentration ratio versus bed volumes for the tracer test. The general trend is very similar in shape to a typical ion exchange calcium breakthrough curve. Also, the steepness of the positive and negative steps on either side of the slug curve qualitatively indicate the absence of channeling.⁴ However, further testing and analysis needs to be performed to fully correlate the absence of channeling; if this test were repeated a number of times with a similar result, it could be said with a high degree of confidence that channeling was mitigated as much as possible.

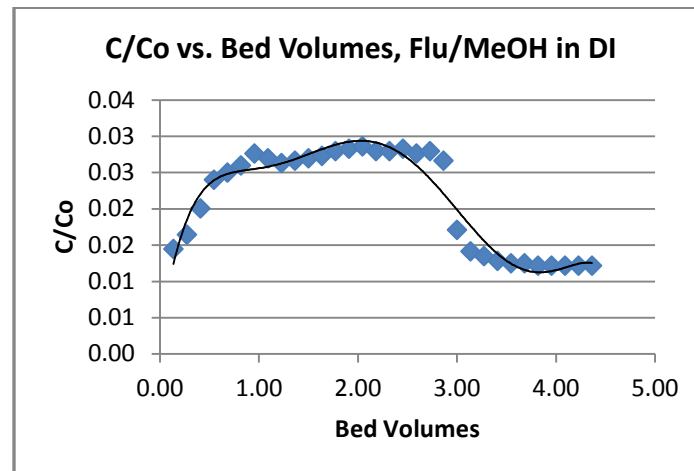


Figure 10. Scaled influent concentration versus scaled throughput for ion exchange tracer testing.

IV. CONCLUSIONS

Based on the results of the equilibrium and sub-scale dynamic column testing, a possible solution for mitigating the calcium precipitation issue on the ISS has been identified. From the original pool of thirteen ion exchange resins, two candidates have been identified that demonstrate substantial calcium removal on the sub-scale. The dramatic reduction in resin performance from published calcium uptake demonstrates the need for thorough evaluation of resins at the low pH and strong oxidizing environment present in the

UPA. The average calcium capacity for the Dowex G26 resin in flight-like subscale testing was 0.51 meq/mL, while preliminary results indicate that the FPC12H likely ranges between 0.72-0.76 meq/mL.

Investigations at a variety of flow rates, length-to-diameter ratios, resin volumes, and flow regimes (continuous versus pulsed) show that changes in physical parameters do not have substantial impacts on resin performance in the very low specific velocity ranges of interest. This result is particularly useful because most commercial applications at higher specific velocities do show a relatively strong relationship between flow and capacity. The lack of a strong relationship will allow more flexibility in the flight implementation of an ion exchange bed for flight. Additionally, this testing indicates that a substantially smaller L/D column can still provide acceptable performance will enable somewhat novel low delta pressure designs with minimal mass penalty.

However, chemical variations in the influent (calcium concentrations and pretreatment dosing) appear to have a noticeable impact on the calcium capacity of the resin. Low calcium concentrations and high pretreatment dosing will likely result in a decrease in calcium capacity. Conversely, low pretreatment dosing will likely result in an increase in calcium capacity. Because both the Dowex G26 and the Amberlite FPC12H are gel-type, hydrogen-form resins with a styrene-divinylbenzene matrix, it is likely that the FPC12H would be susceptible to the same influent chemical impacts as the G26. Verification of subscale tests are recommended to expand the experience with FPC12H prior to implementation in UPA testing.

V. FUTURE WORK

Concurrent to the writing of paper, testing was conducted at the Marshall Spaceflight Center to evaluate a reduced-RFTA-scale ion exchange column in flight-like operations. These 647-mL columns incorporated the Dowex G26 resin and had an L/D of 2.2. The results of this testing will be reported in a later paper, with recommendations on design and operational improvements. Additional subscale testing will be conducted on the FPC12H to determine its performance limitations. Tracer testing will also be conducted to continue the investigation into channeling in an ion exchange column. Finally, if ion exchange is the technology selected for flight development, a stability test will be conducted to determine the vulnerability of the selected resin to long-term exposure to both PTAU and P-Lite. P-Lite is a dilute Oxone/sulfuric acid solution and has been identified as the storage solution for pre-flight packaging of ion exchange resins.

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