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A novel ion exchange system to purify mixed ISS waste water brines for chemical production and enhanced water recovery

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Current International Space Station water recovery regimes produce a sizable portion of waste water brine. This brine is highly toxic and water recovery is poor: a highly wasteful proposition. With new biological techniques that do not require waste water chemical pretreatment, the resulting brine would be chromium-free and nitrate rich which can allow possible fertilizer recovery for future plant systems. Using a system of ion exchange resins we can remove hardness, sulfate, phosphate and nitrate from these brines to leave only sodium and potassium chloride. At this point modern chlor-alkali cells can be utilized to produce a low salt stream as well as an acid and base stream. The first stream can be used to gain higher water recovery through recycle to the water separation stage while the last two streams can be used to regenerate the ion exchange beds used here, as well as other ion exchange beds in the ISS. Conveniently these waste products from ion exchange regeneration would be suitable as plant fertilizer. In this report we go over the performance of state of the art resins designed for high selectivity of target ions under brine conditions. Using ersatz ISS waste water we can evaluate the performance of specific resins and calculate mass balances to determine resin effectiveness and process viability. If this system is feasible then we will be one step closer to closed loop environmental control and life support systems (ECLSS) for current or future applications.

Nomenclature

<i>HCL</i>	=	<i>Hydrochloric acid</i>
<i>NaOH</i>	=	<i>Sodium hydroxide</i>
<i>KOH</i>	=	<i>Potassium hydroxide</i>
<i>Caustic</i>	=	<i>High alkalinity solution (NaOH, K₂CO₃, KOH, and similar)</i>
<i>VCD</i>	=	<i>Vapor Compression Distillation</i>
<i>FOST</i>	=	<i>Forward Osmosis Secondary Treatment</i>
<i>COTS</i>	=	<i>Commercial off-the-shelf</i>
<i>M3Iz</i>	=	<i>A in-house proprietary modified cation exchange resin to perform polyvalent anion removal</i>
<i>L/D</i>	=	<i>Length over Diameter ratio</i>
<i>EQ/L</i>	=	<i>Equivalents per liter (Accounts for ion molecular weight and charge)</i>
<i>BV/hr</i>	=	<i>Bed volumes per hour (non-dimensional flow rate)</i>
<i>ECLSS</i>	=	<i>Environmental Control and Life Support System</i>
<i>IX</i>	=	<i>Ion Exchange</i>

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I. Introduction

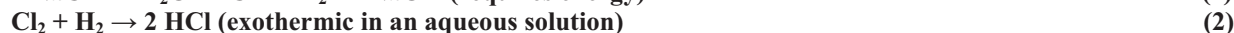
Current water recovery systems aboard the International Space Station utilize vapor compression distillation to realize water reuse potentials of over 70% per cycle¹. Via the use of chromic acid, the waste water (containing urine, humidity condensate, and hygiene water) is pretreated to prevent biodegradation of urea to ammonia and to stabilize any residual ammonia. The resulting waste water is distilled in a rotating device that provides gravimetric separation of vapors from the liquid. This yields a relatively pure distillate stream for further processing along with toxic brine with the majority of the organic, nitrogenous, and salt components of the waste water. No recovery of this brine has been done on Station and only simple dewatering experiments have been done on the ground². Due to the importance of water for crewed space missions and the currently prohibitive mass fractions of water required to visit and habituate extraterrestrial bodies; the marginal increase in water recovery and reuse goes a long way in making these missions viable.

Ground-based next generation water recovery systems have focused on biological pretreatment to lower consumable requirements. Combined with forward and reverse osmosis (such as FOST³), this would yield product water needing less polishing along with brine without toxic chemicals such as chromic acid. As of today, there is no use for this brine except to concentrate it as much as possible and maximize water recovery (with a goal of 95% recovery per cycle).

By the same token, food has been brought on all missions to date and not generated in-situ. Plant growth for food crops has been a continued interest to NASA⁴. Along with water recycling, food production and air revitalization (O₂ production, CO₂ removal) by plants can increase endurance of manned missions to allow travel to Mars and further destinations. Plant growth systems for sustainable manned activities in space is still in its infancy, but the food requirements, as well as the water requirements are prohibitively expensive with current launch systems. Current wastewater recovery processes are not designed to work with hydroponic systems. Plant systems require large amounts of nutrients and water to function. Knowing that all the required plant nutrients can be found in the waste water brine or recovered from plant leaching brines had lead us to consider a system for harvesting this untapped resource. This boils down to a system that can selectively remove key plant nutrients from waste water and extract them in a usable form without the use of consumables while still generating product water.

A novel solution to the above problem is to couple selective ion exchange (IX) resins to a chlor-alkali cell. Contaminants in the brine are removed by consecutive IX resins and the resulting potassium chloride brine is electrolyzed into KOH and HCl. These chemicals are used to regenerate the resins to produce fertilizers among other useful chemical products (consumables for other systems). An upstream system to separate sodium from potassium is also required for plant fertilizer production but will be studied at a later date using electrostatic methods (in line with industrial salt mining)⁵. The end result would be higher water recovery, significant or total consumable generation, as well as the potential to produce a fraction of the fertilizer requirement for sustainable plant growth outside of earth's atmosphere.

For over 100 years the chlor-alkali process has been used on earth to produce useful chemicals from sodium and potassium chloride salts⁶. The basic reaction proceeds as shown:



This process converts the previous "waste product" of sodium (or potassium) chloride into sodium hydroxide (caustic) and hydrochloric acid. This is an electrolysis process using membranes similar to those used in Nafion fuel cells⁶. These chemicals can be used for upstream wastewater pretreatment. Ammonia removal or conversion tends to require alkalinity⁷ while HCl can be used to stabilize waste water in case of process failure. IX resins used for polishing and fertilizer removal from wastewater require HCl and Na/KOH to be regenerated as well. This process basically converts the mass consumable demand into an energy cost which can be supplied by solar panels or similar renewable source. One downside of modern membrane-based chlor-alkali cells is their stringent brine purification requirements. This necessitates highly selective and high capacity IX resins (or other technologies) to purify the brine to specification. In order to reduce consumables, these resins would need to be regenerated and also produce a useful product with the spent regenerate. The purpose of this study is to look into various IX resin technologies in order to identify and solve key contamination issues in the brine stream. If this is possible, this would facilitate chlor-alkali processing as a first step to a closed loop operational Environmental Control and Life Support System (ECLSS). Subsequent research assuming the former is successful would involve maximizing regenerate purity for use in spacecraft crop systems to sustain plant growth and food production.

II. Brine Purification Overview and System Design

Due to the abundance of literature on IX and the synergies it has with the chlor-alkali process, we have chosen IX as the best medium for brine purification. IX is a form of sorption (like absorption and adsorption) that swaps specific ions in solution with active sites on a polymeric matrix (a resin). There are various types of IX resins, with the two major types being cation (positive ions) and anion (negative ions) exchange resins. There are also various chelating resins and resins that absorb both cations and anions. The general IX equation for a strong acid ion exchanger is summarized below:



Due to resin selectivity, the above resin prefers the sodium species and will take it up until it reaches its specific equilibrium concentration. In order to regenerate a specific resin, the chosen counter ion is run through the bed in abundance to reverse the equilibrium and remove the contaminant ion. Usually an excess of regenerate is needed to remove most of the contaminant with the last 10-20% being proportionately more difficult (and not industrially viable) to remove. The regeneration equation is represented as:



Some resins can be regenerated with various dilute acids and bases as well as salts (or even water/steam) as long as the equilibrium can be reversed. Since we are working with brines of a high salt content all of our regenerations will need relatively strong concentrations of acids and bases (> 2M) to reverse their equilibriums. This necessitates the production of KOH and HCl through the chlor-alkali process to be used to regenerate all the IX resins to produce KyXy style fertilizers (such as KNO₃ or K₂SO₄). The resulting weak brine stream from the chlor-alkali process can then be back-recycled for additional water recovery. The above process to essentially upgrade acid and bases lead us to propose a basic system design to facilitate chemical, and eventually fertilizer production from spacecraft waste water. The first step for this system would be to take pretreated (preferably biologically) waste water and separate out the water from the brine. There are multiple ways to do this with vapor compression distillation performed currently but other distillation/osmosis/pervaporation technologies are being developed⁸. Regardless, all of these technologies will produce similar brine at a water recovery rate between 80-95%. The resulting brine would then go through multiple IX resins to remove impurities that would either foul the chlor-alkali cell or produce undesired side-products. This purified brine containing sodium and/or potassium chloride would then undergo chlor-alkali electrolysis under bipolar membranes which would yield an acid stream, a caustic steam, and a weakened brine stream for recycle. It is intended that the acid and caustic streams be used to regenerate the IX resins to produce a fertilizer product and to keep the incoming brine to specification for chlor-alkali. The proposed process is illustrated in Figure 1 below:

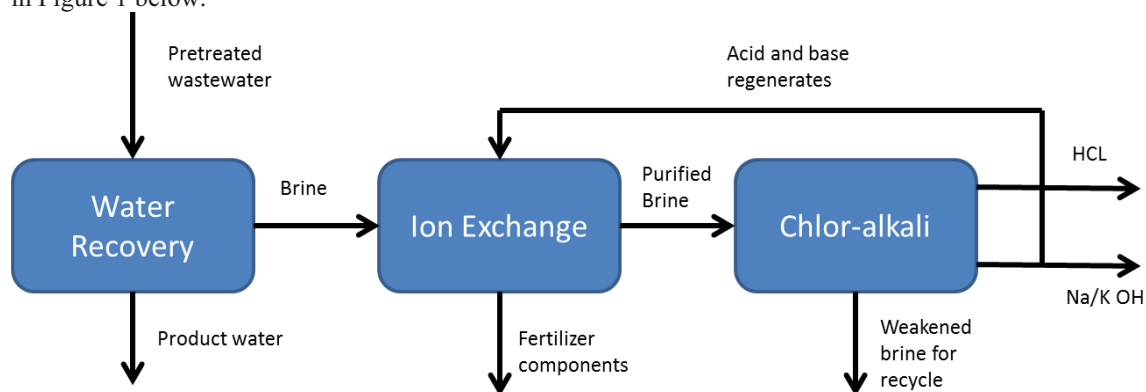


Figure 1. Basic process flow diagram of a brine processing system for ECLSS.

Looking at the expected ion concentration of spacecraft wastewater brine found in⁹ we can plan on what type of ion exchangers are required. With sodium, potassium, and chloride as our main feeds for the chlor-alkali process, we would need to remove the calcium, magnesium, sulfate, and phosphate components from the brine. These contaminants are organized into hardness (calcium and magnesium) and polyvalent anions (sulfate and phosphate) which each have classes of resins available for use either commercially or experimentally. Depending on the

ammonia removal system there can be nitrogenous species present in the wastewater brine: ammonia (assuming water recovery rejection), or nitrate (nitrification). For this study, we assumed a brine without nitrogen and for specific cases considered nitrate-containing brines (for nitrate removing resins). Organics in the brine are low due to carbon oxidation biochemical reactions performed in pretreatment, so organic removal is also not considered in this work.

The above requirements led us to propose the use of a series of multiple IX beds to realize the required brine specification for chlor-alkali processing. A form of brine separation, which can isolate the sodium and potassium fractions, is needed if KOH is required to be generated separately from NaOH. This process is out-of-scope for this document but will most likely involve a form of brine-drying and electrostatic separation of the resulting crystals. These crystals could then be re-dissolved to an optimal concentration for IX and chlor-alkali processing. The biggest barrier to chlor-alkali longevity and operation is the removal of divalent cations (hardness)⁶. The first IX bed would most likely be a cation exchanger designed specifically for their removal. Next would be an anion exchanger designed specifically for the removal of polyvalent anions. It is possible this may require two separate IX resins and this would only be needed if acid quality is important. If nitrate is present in the brine then another anion exchange resin would be required to remove the nitrate from the chloride brine. This is shown in Figure 2 below:

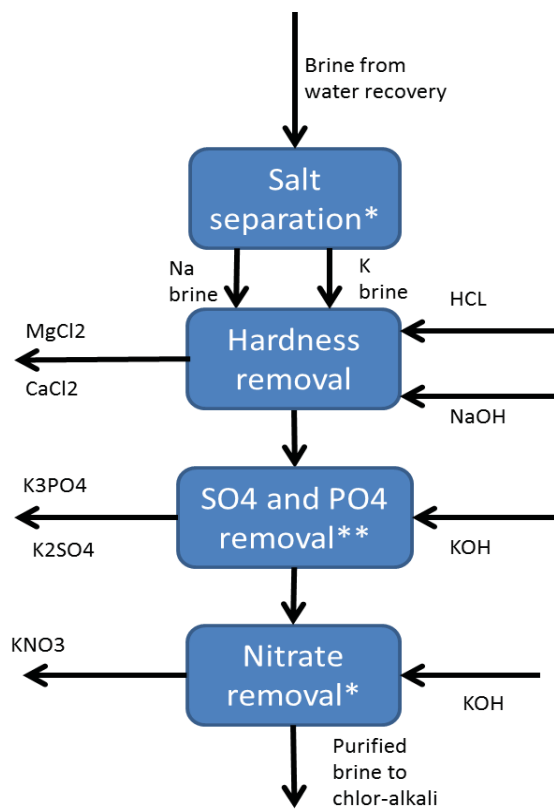


Figure 2. Breakdown of Ion exchange steps including salt separation.

** = optional if not producing fertilizer*

*** = optional if acid can be mixed hydrochloric/sulfuric/phosphoric*

With the proposed steps above, we must generate requirements in selecting candidate resins for the unit operations. The specific requirements are:

- Candidate resins must have high selectivity and capacity for their target ion.
- A resin duty cycle with a candidate resin should minimize leakage of the target ion and minimize the rinse requirement per unit of purified brine.
- Candidate resins must minimize capture of “product ion” (Na, K, Cl).
- Candidate resins must be regenerated with consumables generated from brine (acids, bases).
- Candidate resins should produce a regenerate effluent useful for plant systems or at least another sustainable activity.

- Candidate resins should have a high resistance to osmotic stress and survive potentially 1000's of duty cycles.
- Candidate resins should have kinetics that are fast enough so that large amounts of resin volume, in relation to brine volume, are not required.
- Candidate resins should not introduce contaminants for the chlor-alkali processing (organic residues, fines).

III. Materials and Methods

A. Brine specifications:

Spacecraft waste water and resulting brines have been well characterized by Verosko and others⁹. The brine recipes chosen for this experiment are based off the solution 2 (12% urine, 16% humidity condensate with balance hygiene water) recipes for ersatz waste water from⁹ (see figure 3). We took the inorganic fractions from these recipes and concentrated them to simulate 90 - 95% water recovery (5-10% of the water remains in the solids fraction). Some resins and experiments required the preparation of modified brine recipes (for example simulating upstream nitrification or upstream ion removal). All brine solutions were prepared in one liter increments and used ultrapure water in their dilution.

Ion (ppm)	Na	K	Ca	Mg	Cl	PO ₄	SO ₃	NO ₃
90% recovery w/o N	10000	10000	250	250	25000	5000	5000	0
90% recovery w/ N	10000	20000	250	250	25000	5000	5000	30000
95% recovery w/o N	20000	20000	500	500	50000	10000	10000	0
95% recovery w/ N	20000	40000	500	500	50000	10000	10000	60000

Figure 3. Approximate brine concentration in ersatz brines produced.

B. Resin specifications:

Unless otherwise noted, all resins were procured from Dow chemical through Octochem sample fulfillment services. All volume calculations use the manufacturer's listed shipping weight density. Two other Resins were procured from Layne Christensen and company (Layne RT and Layne RTSW).

C. Regenerate specifications:

Analytical grade NaOH, KOH, and HCl were procured from Sigma Aldrich. Care was taken when making caustic solution to evacuate air from the solid NaOH/KOH to prevent the hygroscopic prills from absorbing water and causing lower than expected concentrations. All regenerate solutions were prepared by the liter and used ultrapure water in their dilution.

D. Equilibrium (batch) studies (and kinetic studies):

To gather initial kinetics data and down select resin candidates, equilibrium studies were performed. The basic procedure was taken from a Dow testing document¹⁰. A ladder of centrifuge tubes is prepared with increasing amounts of resin, with a static amount of brine, and left to mix under rotation (ATR RKVSD rotamix) for ~24 hours to reach equilibrium. By measuring the brine before and after the treatment, capacity and selectivity can be determined. In addition, various operating conditions can be attempted in parallel at minimal analytical and chemical expense. Removing duplicate brine/resin tubes from rotation, a ladder at a time, produces capacity and selectivity as a function of contact time. This data is useful for scaling up for eventual column utilization.

E. Column (continuous) studies:

Once operating conditions can be derived from equilibrium studies, columns can be sized according to treatment ratio and expected test flow rate. All columns are built out of Harvel[®] clear PVC and are terminated with polypropylene NPT John Guest fittings to allow adaption to ¼ inch connections. The weighted amount of resin is secured using retention rings along with 200 and 400 stainless steel meshes. Column absorption (loading) and regeneration are performed to Dow's column testing document¹¹. All columns have a 100% safety factor in length

to allow sufficient freeboard for resin expansion which can be up to 30% for some resins. This also prevents channeling when operating under downflow conditions.

Once a column is filled with resin, it is rinsed and sealed with mesh on both sides. Before an experiment, the pump (FMI Lab Pump Model RHV) is primed with the correct brine or regenerate and calibrated for the flow rate dictated by the experiment. Once flow begins, aliquots are taken after a specified amount of bed volumes until it is predicted the column has broken through and reached influent brine levels (usually double the calculated breakthrough volume). After that, the column is left to sit for at least an hour, flipped, and run for regeneration using the same above steps. Rinse samples are usually taken to sample the liquid around the resin before any absorb or regeneration cycle. After every complete cycle the column is rinsed around two bed volumes to “reset” it.

F. Column optimization

The purpose of the column study is to evaluate the resins under realistic conditions in an ECLSS architecture. The main performance metric for the column study is the number of bed volumes treated before breakthrough. The selectivity of the resin to the target ion, compared to other ions, is also important. Column parameters (influent pH, contact time in BV/hr, column upflow/downflow) are modified to delay breakthrough and maximize the total usable capacity. Figure 3-4 documents this breakthrough curve with “A” being the usable capacity before breakthrough and “B” being the unusable capacity that exists post-breakthrough. “A+B” should be equal to the stated resin total capacity. Decreasing the flow, especially for kinetically limited resins, tends to increase the ratio of A/B and makes it more viable for our system design; however, longer contact times equal more resin investment (more equivalent system mass).

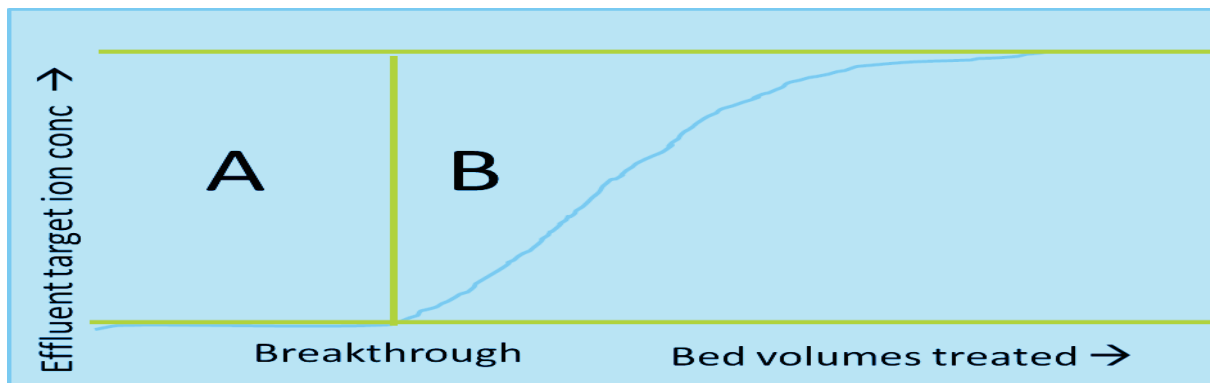


Figure 4. Breakthrough curve of hypothetical ion exchange column.

G. Total Organic Carbon (TOC) and Total Nitrogen (TN)

For analysis of TOC and TN, samples were collected, and analyzed within one week. Samples were run in triplicate for quality assurance and analyzed using an Apollo 9000 TOC/TN (Teledyne Tekmar) analyzer with TOC Talk 4.5 Software. This instrument uses a combustion method to convert carbon-containing molecules to CO₂. The carrier gas then sweeps the resulting gas into a non-dispersive infrared detector (NDIR) where the concentration of CO₂ is measured. A quantification range of 10 to 750 mg/L was used for all samples. Certified total organic carbon standard and total nitrogen standards (Ricca Chemical) was used for calibration.

H. Ion Chromatography (IC)

A dual Dionex ICS-2100 system (Dionex, Sunnyvale, CA, USA), configured to simultaneously analyze anions and cations, equipped with a conductivity cell (DS6), vacuum degasser, column heater, eluent generator, and self-regenerating suppressor (Dionex ASRA 300 4mm and CSRS 300 4mm) was used for the work. For the analysis modified EPA Method 300.1 was employed. Separation was achieved on a Dionex IonPac AS18 and IonPac CS12A column (4×250mm) isocratically using 32mM Potassium Hydroxide and 20mM Methanesulfonic Acid, both

with a flow rate of 1mL/min and column temperature of 30°C. Samples (25µL injection loop) were introduced to the column by an autosampler (Dionex AS-DV autosampler) using 5mL sample vials. Certified anion and cation standards (Inorganic Ventures) were used for calibration.

I. Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. Samples were analyzed according to EPA Method 200.7. This method is a consolidation of existing methods for water, wastewater, and solid wastes. Single element certified standards used to calibration (Environmental Express). Samples collected and immediately analyzed using an IRIS (Thermo Scientific) ICP-OES.

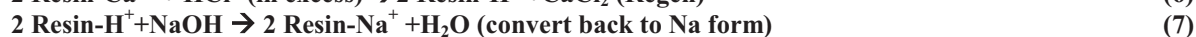
IV. Results with Specific Resins for targeted ion removal

Various resins were selected or recreated from the literature in order to test their ability to selectively remove the target ion from salt-heavy brine. For brevity, only the best runs and conditions will be shown for each resin type

A. Hardness removal via chelating resins

The main source of fouling in chlor-alkali membranes is due to hardness values made up of mostly calcium and magnesium. These divalent cations form insoluble masses on the membranes that require acid etching to remove and contribute heavily to cell lifetimes. For our spacecraft chlor-alkali system it is paramount to remove these values constantly and regenerate at minimal consumable costs. Most chlor-alkali plants see around 1-20 ppm hardness in their evaporator salts concentrated brine⁶. However ECLSS waste water brine hardness is measured in the 100's of ppm, with monovalent salts only a fraction of the fully concentrated. This will require less selectivity of the resin for hardness removal but capacity will be more important due the high amounts of hardness.

Resins were developed for this specific process since it is a problem shared by industry. These chelating macroporous resins utilize aminophosphonic active sites to form complexes with multivalent cations. This allows extremely high selectivity for divalent over monovalent cations and also facilitates the regeneration using hydrochloric acid which is produced by the chlor-alkali process. Starting with the sodium form the reactions are:



Amberlite® IRC747 (Dow Water and Process) was chosen due to its improved kinetics, selectivity, and throughput compared to other chelating resins¹². Using the average brine values and the resin's specification sheet, it was determined that between 30-300 mg resin would be added to 10ml, 90% recovery full brine (brine 1) in 30mg aliquots for a total of 10 samples with one negative control. These samples were treated according to the established equilibrium study procedure then regenerated first with 2M HCl, then with 2M NaOH with rinses in between. Figure 5 indicates the hardness removal as a function of treatment ratio:

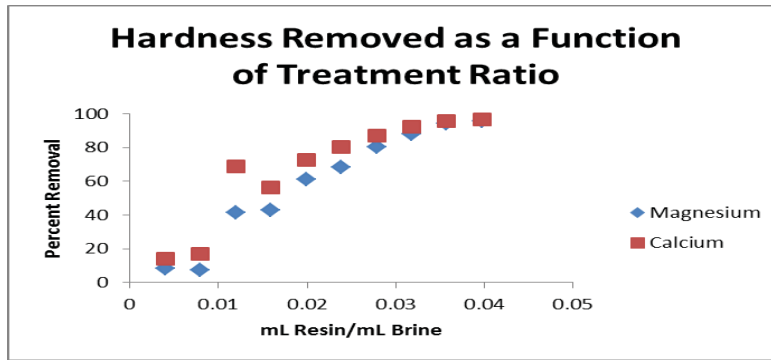


Figure 5: Equilibrium hardness removal as a function of volumetric treatment ratio.

This equilibrium study indicated that a treatment ratio of around 30:1 could be expected and gave us initial conditions to test column studies. After 5 column studies (not shown), it was found that the best results were found using a ¼ inch ID column with 3.6:1 L/D ratio run under downflow (prevents channeling) at 15 BV/hr absorption and regeneration (half the flux the spec sheet recommends). The breakthrough curve under best conditions (figure 6) shows minimal hardness breakthrough until around 22.5 bed volumes of resin followed by a steep rise in effluent hardness (higher than the influent which indicates dumping of ions) which shows good kinetics. Regeneration of the resin (Figure 7) with 2M HCl shows almost complete hardness recovery (over 80%) within 4 bed volumes of acid (conversion to active form with NaOH not shown). Right before breakthrough near 1.4 total EQ/L hardness was attached to the resin (compared to 1.75 total EQ/L on the spec sheet) which indicates around 80% of the resin was occupied by hardness ions which yields a gross selectivity near 200:1 (5:1 ratio on the bead with a ratio of 40:1 monovalent: divalent cations).

pH of the influent brine was measured near 4.5 which is near the minimum recommended pH for running this resin. Previous studies (SOURCE) have shown deteriorated performance at low pH's like those found with brines containing chromic and sulfuric acid. However, near neutral pH, the performance of this resin (in both capacity and regenerability) seems ideal for use in a spacecraft ECLSS system.

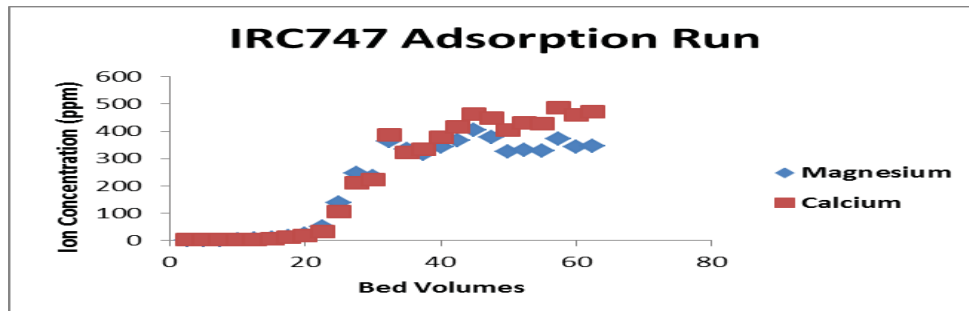


Figure 6. Breakthrough curve for IRC747 under best conditions.

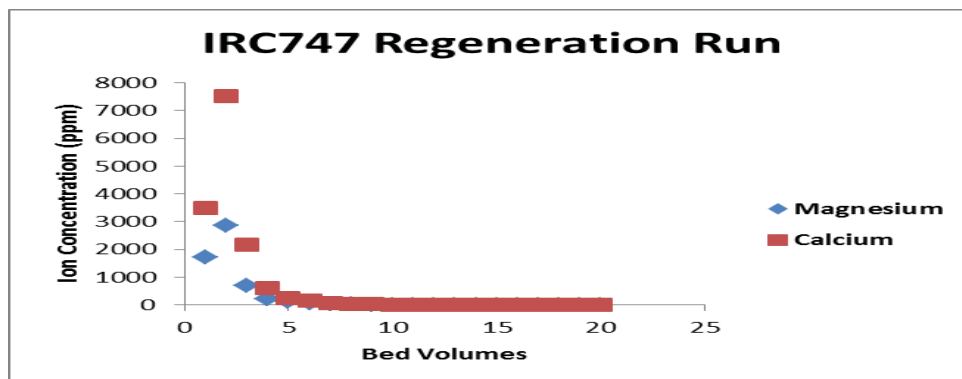


Figure 7. Regeneration of IRC747 using 2M HCl.

B. Sulfate removal using zirconium impregnated resins

Sulfate contamination is a known issue in terrestrial chlor-alkali plants with multiple removal schemes implemented⁶. In most industrial implementations, high sulfate levels in the brine get recycled and build up until efficiency and membrane life decrease below acceptable limits⁶. Bipolar electrolysis would yield a mixed hydrochloric/sulfuric acid mix which would have ramifications if used for upstream IX regeneration¹³. Since specifications for what type of chlor-alkali membrane cell will be utilized for spacecraft consumable generation are TBD, it would be good to evaluate sulfate removal technologies if they are required for operation.

Hydrous zirconium oxide is well known for its IX properties, especially as a hybrid ion exchanger¹⁴. As a function of pH, it goes from an anion exchanger at a pH below 3 to a cation exchanger at a pH above 12¹⁴. In chlor-alkali plants the hydrous zirconium oxide is added to a brine tank to mix with the sulfate under low pH and the solid is removed and added to a caustic tank to pull off the sodium sulfate for disposal⁶. This is described in the reactions below:



Another implementation of hydrous zirconium oxide is to fix it to a cation exchange resin. Soaking a macroporous sulfonic acid group cation exchanger in zirconyl chloride and using ammonia, can fix the zirconium hydroxide functional groups onto the resin and still maintain its hybrid ion exchanging properties¹⁵. With the uniformity and process characteristics of the base resin, this allows improved usability and better kinetics without any filtering steps. This sulfate removal method was evaluated against the ersatz waste water brines under different contact times and pHs. The main goal was to remove the vast majority of the sulfate values from the brine without too much co-sorbing of chloride. Also any cation exchange capacity (from either the zirconium or the base resin) would need to be minimized or at least characterized. The optimal contact times and consumable requirements (for pH control and regeneration) will be calculated and used to evaluate this resin for spacecraft usage.

A suitable macroporous cation exchanger in Dowex[®] M31 was procured. This version was a Monosphere[®] which gives a uniform (instead of Gaussian) particle distribution that fits between a 400 and 650 mesh screen. A portion of this M31 was modified to yield M31z. This procedure is similar to the one performed by Bauman et al.¹⁵ but performs the soaks over longer durations under stirring and not column flow. After rinsing the finished product, the effluent was screened for zirconium via ICP-OES to confirm the resin has been sufficiently rinsed.

Initially, two equilibrium studies were performed to gauge the performance of this modified resin compared to the control. The first study involved using the conditions found in the original documentation (pH 1.5 brine using water regeneration) while the second study used more traditional anion exchange conditions (pH 4.5 brine using 2M KOH regeneration). A ladder of five resin volumes was added to 10 ml of the above brines and left to rotate for 24 hours following standard procedures. These equilibrium studies were performed using 95% water recovery brines.

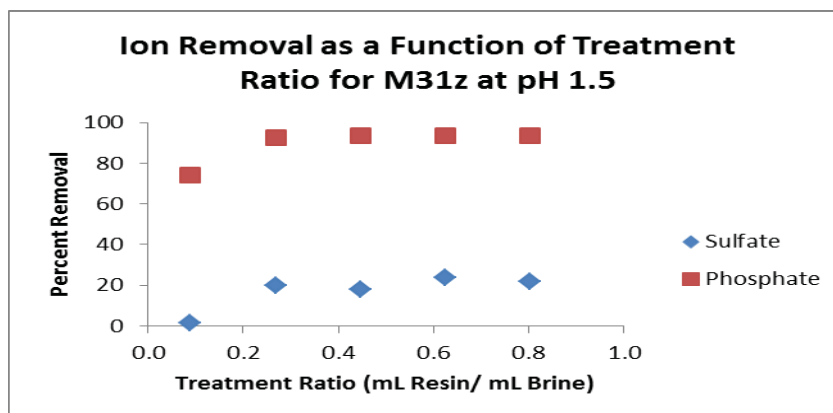


Figure 8. Ion removal as a function of treatment ratio for M31z at pH 1.5 for 24 hours.

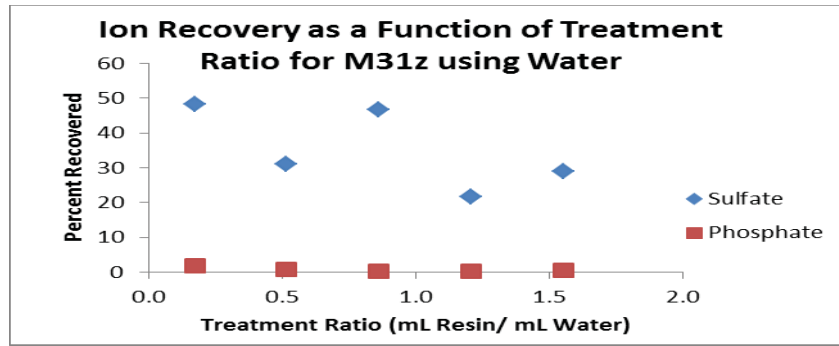


Figure 9. Ion recovery as a function of treatment ratio for M31z using water for 24 hours.

At 24 hours of contact time and at a pH of 1.5 (Figure 8), phosphate was almost completely removed at 10:1 brine: resin ratio, while sulfate removal was never above 20% due to phosphate competition. However, when the resin was regenerated with water, near a neutral pH, only sulfate was recovered (Figure 9). When the absorption was repeated at a pH of 4.5 brine (Figure 10) phosphate absorption was unaffected while sulfate absorption was completely eliminated. When regenerating this resin with 2M KOH (Figure 11) phosphate was eluted readily to completion. This indicates that a system could be built to take advantage of phosphate removal at higher pH's (with regeneration with KOH) then the resulting brine can be acidified and treated with the same resin for dedicated sulfate removal (with no phosphate completion) and regenerated simply with water.

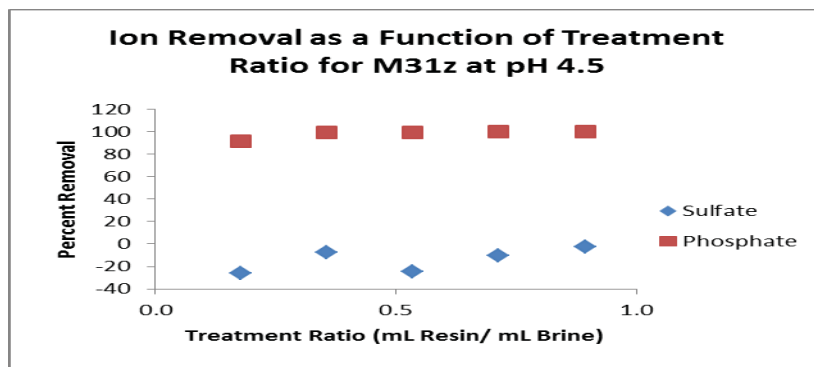


Figure 10. Ion removal as a function of treatment ratio for M31z at pH 4.5 for 24 hours.

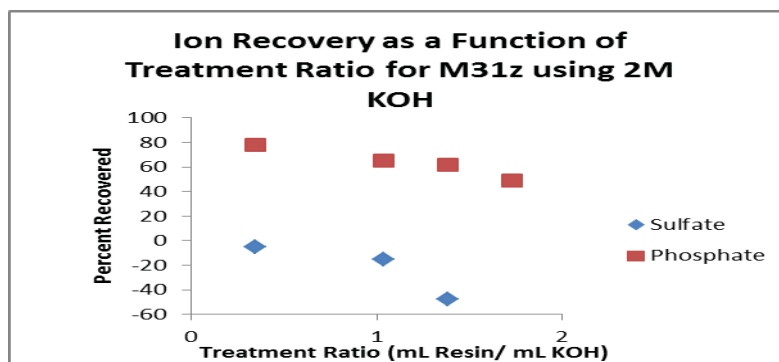


Figure 11. Ion recovery as a function of treatment ratio for M31z using 2M KOH for 24 hours.

Column studies were performed with various brines (some missing sulfate or phosphate) and various contact times and pHs (not shown), but results were poor due to low contact time (30 minutes). Batch tests performed from 30 minutes to 24 hours indicated that the kinetics of this resin are quite slow (more than an hour to reach equilibrium) and will require large resin beds to make the separation and/or higher temperatures (also not shown). Even with these limitations, this unique resin shows very large promise for the use of sulfate and phosphate removal from concentrated brine streams.

C. Phosphate removal using iron nanoparticle impregnated resins

Ion exchange is not traditionally used for phosphate removal. Most types of anion exchange resins have extremely poor selectivity for phosphate over chloride or any other anion. However, recent developments have been made using hybrid ion exchangers that are selective for phosphate. Ferrous oxide nanoparticles are produced and then irreversibly loaded onto a parent anion exchange resin. Under near neutral pH (6-8) the selectivity for phosphate over chloride or sulfate is around 50:1¹⁶. The main purpose of this resin is for phosphate and arsenic removal for wastewater or drinking water: reducing the concentration from a handful of ppm to under 100 ppb. A company has licensed this technology (Layne Christensen) and sells it commercially under the Layne[®] RT brand.

By using a hybrid anion exchange resin for selective phosphate removal, this can allow nutrient recovery by regenerating the resin with KOH to produce potassium phosphate.



To evaluate this new type of resin, Layne[®] RT and Layne[®] RTSW were procured from Layne Christensen and company. The parent resin Dowex Tan-1 was also procured from Octochem sample fulfillment services. To screen the resin for useful phosphate selectivity, an equilibrium study, using a ladder of resin amounts in a fixed amount of brine, was performed following standard procedure (not shown). Once the resins were found to have the ability to remove phosphate; columns were constructed based on anticipated treatment ratio and resin capacity to generate a breakthrough curve for evaluation. Column runs would be performed under various contact times, orientations, and with specific brines to simulate downstream processing.

It was found that the best performance for Layne RTSW (or any other of the tested resins) was using downflow operation in a high L/D ratio column at 4 BV/hr for both absorption and regeneration, with the latter using 2M KOH. Figure 12 indicates the breakthrough curve with the various ions, with sulfate and chloride breaking through around 5 BVs while phosphate takes over 10 due to the resin's selectivity. Regeneration of the resin effectively went to completion near 4 BVs using 2M KOH (Figure 13). Gross selectivity on the resin was poor with the majority of the active sites taken up with chloride and only 1 EQ/L effective capacity was found for phosphate (Figure 14). This means that during regeneration the potassium phosphate solution will be contaminated with a large fraction of chloride which could lead to plant toxicity if used as a fertilizer. Further efforts need to be taken to either improve phosphate selectivity or at worst be able to selectively elute them from the resin (such as using a pH gradient). From these tests it seems that if the kinetics issues can be solved for M31z then it would be a more effective resin.

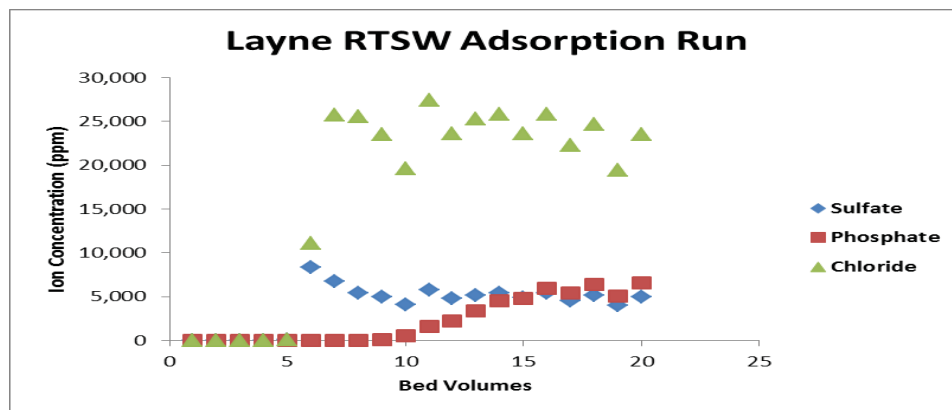


Figure 12. Breakthrough curve of Layne RTSW.

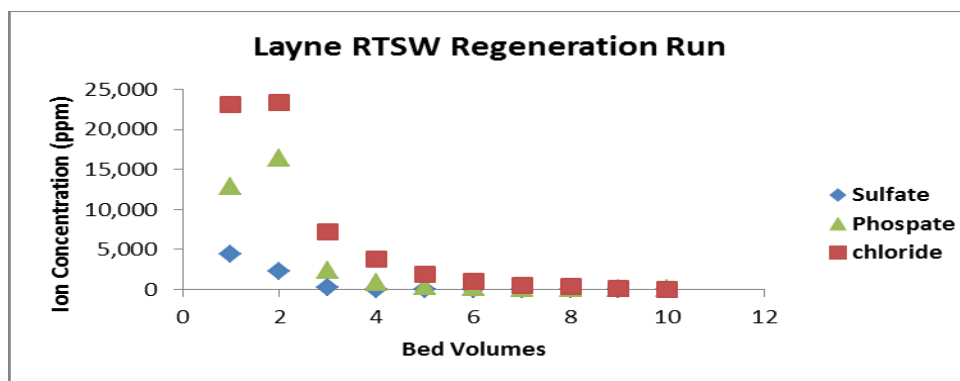


Figure 13. Regeneration curve of Layne RTSW.

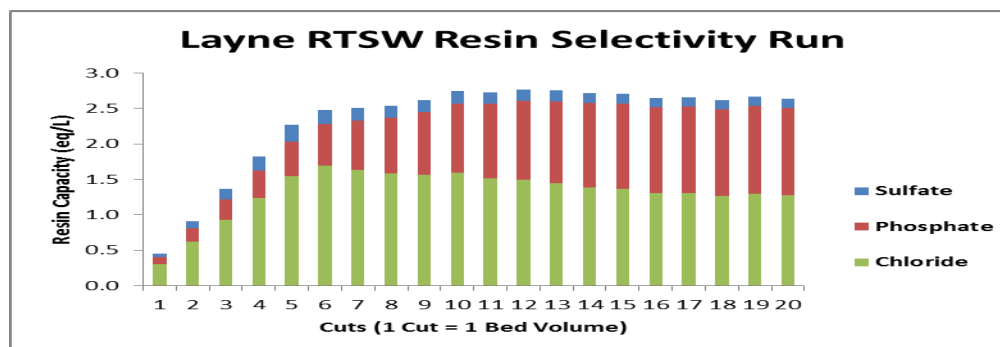


Figure 14: Selectivity of ions for adsorption of Layne RTSW.

D. Nitrate removal using modified and COTS resins

Potassium Nitrate (KNO_3) is commonly used as plant food and fertilizer. Isolating the nitrate in the wastewater brine through IX and then bonding the nitrate with potassium produces one of the key nutrients. Other anions are present in the brine and must be removed prior to the nitrate removal or ignored by the “nitrate” resin as in the case of chlorine. The ability of a resin to complete this process is based on several key factors: the resins affinity for a particular ion, the concentration of that ion, and the concentration of other constituents ions that can be adsorbed by the resin. All of these factors have strong influence over a resins capacity, and efficiency to remove or adsorb the target ion.

Amara^{17,18,19,20} has published papers examining the effect of fixating polyethyleneimine (PEI) to anion exchange resins for the purpose of enhancing selectivity towards nitrate while rejecting chloride ions. PEI is a branched polyelectrolyte. Amara formulated a method for fixating the PEI to the resin, and conducted equilibrium studies to qualify selectivity of the resin towards nitrate^{17,18}. The paper claims that the PEI modification enhances nitrate selectivity and rejects chloride ions. Several hypotheses are given to explain the phenomenon. Reduction of resin porosity, modification of the hydrophilic/hydrophobic balance both are sound explanations for the change in characteristics of the resin. Sigma-Aldrich also states that PEI provides a greater degree of hydrophobic character. This tends to improve adsorption of ions with polar qualities such as nitrate. Amara’s papers could only speculate as to the quantity of either chloride or nitrate in the water after IX; however his results showed an enhanced selectivity for nitrate and a reduced affinity for chloride.

Two resins, Amberlite IRA900 and PEI modified IRA900 were tested for their ability to adsorb nitrate while ignoring other anions, particularly chloride. An equilibrium study was conducted first to get a sense of the resins capacity and selectivity towards nitrate, and to examine the effects of the PEI resin modification. Next, column testing was used to find the breakthrough curve of nitrate in the brine. Column design parameters were based on the results of the equilibrium study. The breakthrough curve of nitrate is ultimately what the study is trying to examine. To be successful several bed volumes of brine should be passed through the column prior to break though. Once break through has occurred the column run is over and the resin must be regenerated with a basic solution (2M KOH). This is described in the reactions below:



Note that this reversible reaction concentrates the nitrate into the regeneration stream allowing the remaining KCl (at elevated pH) to undergo electrolysis to form the KOH needed to regenerate this column. Parameters to be optimized (beside the breakthrough point) include general resin capacity, selectivity, and regeneration efficiency (unit nitrate liberated per unit caustic potash). Variables under consideration include loading rate (bed volumes/hr) and brine composition (either normal “full” brine or a Cl/NO₃ binary brine with full cation compliment). The modified resin, another COTS anion exchange resin (TAN-1) and the unmodified resin (as a control) will also be tested.

IRA900PEI was created according to the procedure outlined in¹⁶. It was estimated that around 2 bed volumes of brine could be treated before breakthrough. This led to a creation of a ladder of 10 samples (0.5 to 5 ml) of treated and untreated resin added to individual 10 ml 90% recovery brine tubes. An equilibrium study with a duration of 24 hours, using the procedures mentioned above, while regenerating with 2M KOH, was performed. After removing the depleted brine, the samples were subsequently regenerated for 24 h using 5 ml of 2M KOH for each sample (yielding 1-10 treatment ratio of resin to regenerate) with the resulting effluent analyzed to determine how much of the nitrate removed was eventually recovered. The results (not shown) yielded an expected treatment ratio of below 1, which would make an effective system design almost impossible. However when using IRA900 in the chloride form (instead of hydroxide) there was some selectivity and capacity improvements (Figure 15) with near 4 bed volumes able to be treated. Regeneration however (Figure 16) was poor but selectivity (Figure 17) was better with almost 2:3 of the resin trapping nitrate yielding an approximate selectivity of 1.5:1 (better than any other column study performed (not shown)).

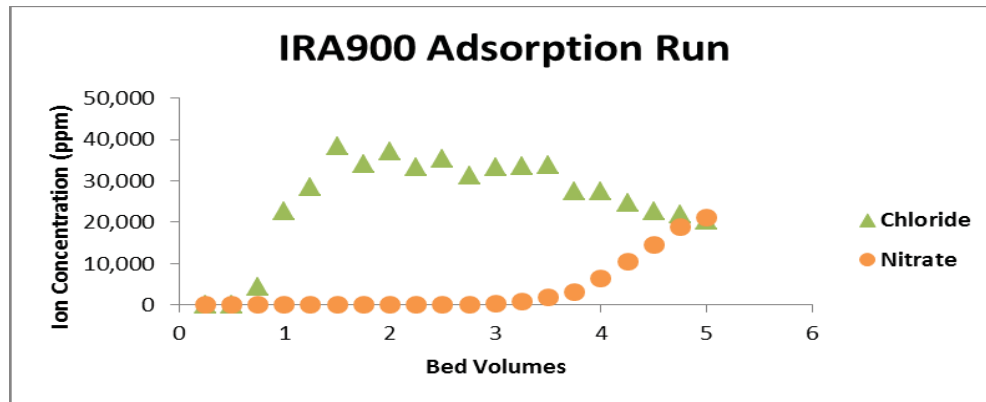


Figure 15. Breakthrough curve of IRA900 under chloride form.

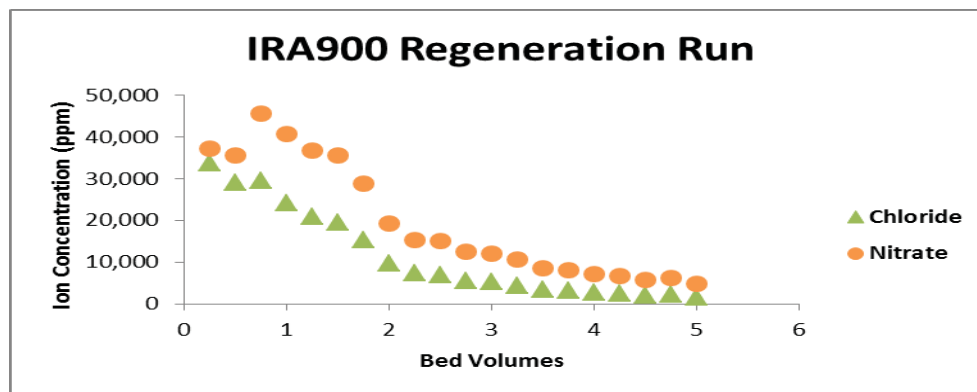


Figure 16. Regeneration of IRA900 using 2M KOH.

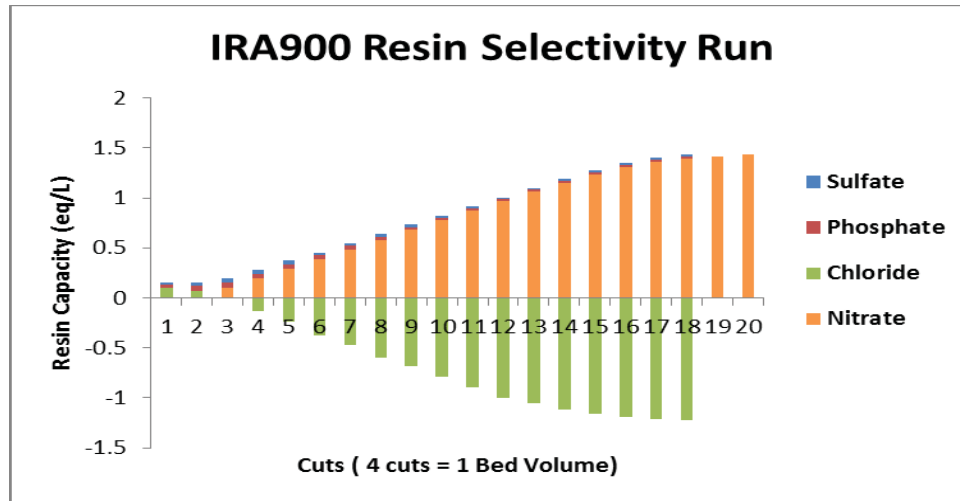


Figure 17. IRA900 selectivity for various anions during absorption.

Even though this separation may not be feasible in its current implementation, there can be further improvements in nitrate selectivity and capacity to allow this system to trade better.

V. Proposed system designs

After evaluating various IX resins for brine purifications, it seems that most if not all the original goals are possible. Assuming biological pretreatment is performed which converts the vast majority of nitrogen to nitrate (via nitrification); then Architecture “A” below (figure 18) would be the appropriate IX train. If plant systems were in use, the influent brine would need to be segregated for sodium and potassium and either processed in alternating batches or by having two parallel trains of resins. The main change from the proposed system design is the use of M31z as both a phosphate and sulfate recovery resin due to the exploitation of the resin’s selectivity and kinetics as a function of pH. At slightly less acidic pHs only phosphate is removed from the resin (at long contact times) while at very acidic pHs sulfate is removed (so is phosphate, but it would be gone by the third stage). This simplifies design and maximizes the use of M31z’s very large capacity and selectivity for polyvalent ions.

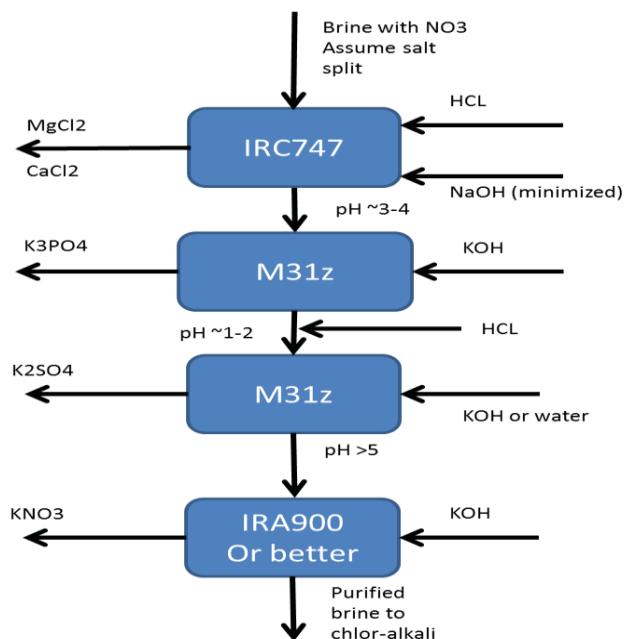


Figure 18. Proposed system architecture “A” for use with biological nitrification pretreatment.

Due to the last (nitrate removal) stage being the least efficient in removing nitrate over chloride and by having the highest consumable requirement per unit brine treated, it would be better to avoid nitrate production if nitric acid would be undesirable (which is true for resin regeneration). By using non-biological ammonia removal processes such as struvite precipitation⁸ (requires caustic) this would reduce consumable demand and increase product chlorides. Struvite is currently envisioned to operate before water separation⁸ so the IX train for architecture “B” (Figure 19) would be simpler. Struvite requires alkalinity to operate but recovers the wet ammonia vapor using low quality heat and vacuum. Regardless the alkalinity used for struvite would be recovered in the waste brine. Producing ammonia instead of nitrate allows use for sustaining refrigeration working fluid on spacecraft while still producing an adequate fertilizer.

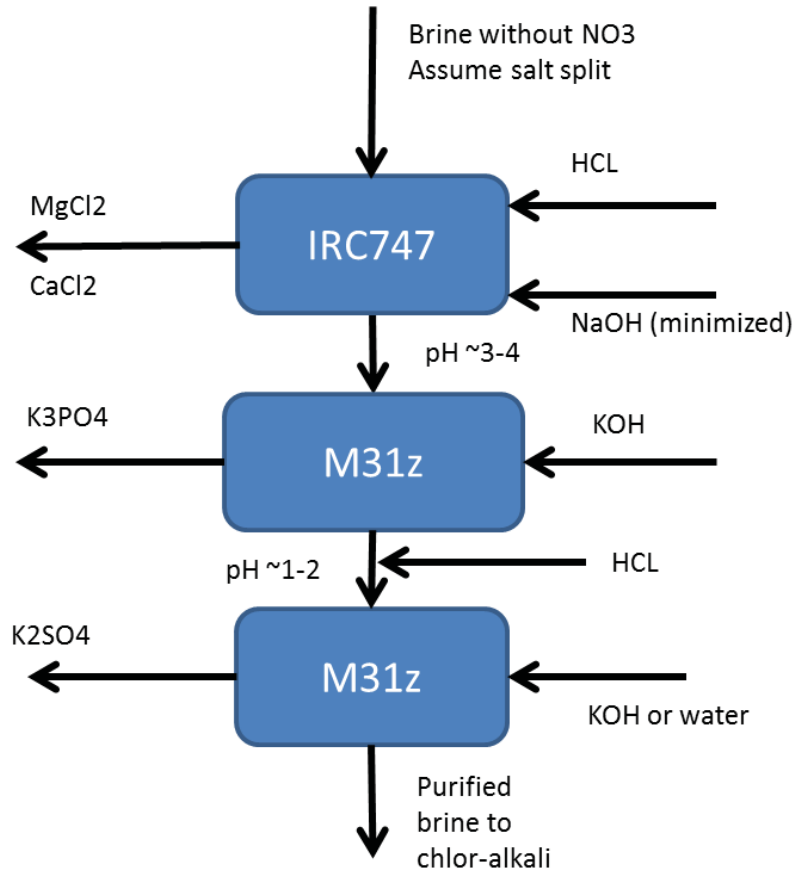


Figure 19. Proposed system architecture “B” for use with ammonia sequestering pretreatment.

The previous two architectures focus on producing fertilizers as well as other consumables while increasing water recovery. However it could be many years until gravity independent plant growth systems are viable for spacecraft or off world colonies. Consumable requires for current waste water recovery systems are high enough that chlor-alkali could still be valuable for the increased water recovery and chemical production alone. This could be achieved by simply running IRC 747 resin in front of the chlor-alkali cell to produce a mixed acid and base product as well as a weakened brine stream (not shown).

Using the “B” architecture and current ISS waste water specs (~10 L per person per day with six people on board) remove: we proposed a back-of-the-envelope calculation to see if it’s viable. With the collected data from the individual resin tests (mostly breakthrough point, 80% recovery point, and required contact times), columns were sized for a daily IX purification of the waste water brine assuming 90% water recovery and upstream ammonia removal. Figure 20 summarizes the key specifications envisioned.

Stage	Resin	Amount	Load rate	Regen rate	Rinse	Influent pH	Effluent pH
1	IRC747	300 ml	2 BV/h for 10 hr	2 BV/h for 3hr	2-1BV/h rinses after each half-cycle	4-10 (might need base)	variable
2	M31z	600 ml	1 BV/h for 10 h	1 BV/h for 6h	2-1BV/h rinses after each half-cycle	3-6 for P removal	High
3	M31z	600 ml	1 BV/h for 10 h	1 BV/h for 6h	2-1BV/h rinses after each half-cycle	1-2 for S removal (HCl)	High

Figure 20: Tentative specification sheet for architecture “B” for ISS waste water brine purification.

Even at very long contact times (30-60 minutes) the size of each resin column is almost trivial. Unlike most industrial systems, contact time isn't a forcing function for this design since our treatment flux is only 6 L / day. This allows slow resins like M31z to shine and realize their high capacity and selectivity. At the currently selected sizes, the brine would run through all the columns in series at 10 ml/min without the need for intermediate holding tanks and more liquid/vapor separators. After a 10 hour load cycle (note that not all beds would be full to allow for sufficient safety factor), each column would be individually regenerated in parallel (or series if pump allotment dictates) for 3-6 hours. Before and after regeneration, there would be a short rinse period with clean water that would subsequently be back-recycled to pre-water separation (not shown in drawings). This would leave 6 hours in the day for the IX train to idle which is approximately the time required for most water separation activities to commence (distillation, FOST). Increasing the size of the columns would reduce the daily duty and increase idle time which could be useful depending on the chlor-alkali running times (most likely only a few hours a day due to specific brine flux).

Brine processed per day	6 L at 90% water recovery
IX system loading flow rate	10 ml/min for all resins using one pump
IX system regen flow rate	10 ml/min for all resins using one pump/3 heads
IX total duty cycle	18 hours with 6 hours idle
Acid demand	1.8 L 2 M HCl plus IX titrant plus water separation demand
Caustic demand	7.2 L 2 M KOH plus IX titrant plus ammonia removal demand

Figure 21. Key parameters for architecture “B” implementation.

The table (Figure 21) above gives some key parameters for this implementation. The main ones of concern are the acid and caustic demand of the regeneration cycles for the included resins. An influent brine concentration of approximately 0.25 M K and 1 M Cl, assuming extremely high chlor-alkali recovery, would only generate less than a liter of 2M KOH and 3 L of 2M HCl a day. This would not meet the caustic requirements, so some action would need to be taken, especially if excess acids and bases are needed for other applications. With current calculations, there seems to be a surplus in acid so it would be feasible to allocate some to water recovery pH control (to increase trace ammonia rejection for RO membranes and for emergency waste stabilization). The caustic shortfall can be solved by better caustic utilization in regeneration or by “priming” the system with extra salt to close the loop.

Performance of the system as whole can be increased by achieving higher selectivity and/or capacity of the specific resins (either through resin modification or optimization of conditions). Further studies would need to look into more optimization of flow rate (to take advantage of high available contact time) and pH sensitivities (which can yield vastly different performances). If waste heat can be found and utilized this can increase the kinetics of the IX and yield better performance. Regeneration can also be optimized, especially through chromatographic methods to better utilize the regenerate and concentrate the target ion.

VI. Conclusion

Ion exchange resins (combined with chlor-alkali electrodialysis) can yield valuable products to enable plant growth in ECLSS. With improving resin technologies, allowing higher selectivities and more purified products; chlor-alkali looks like a likely candidate to close the loop for plant growth systems. With enough available power, chlor alkali can also act as a one-step water production system²¹. Instead of brine production, an aqueous acid and

base stream would be made which can produce the above mentioned fertilizer components; or combined to form a concentrated brine stream for further integration with brine dewatering technologies. Even outside of ECLSS these technologies look viable for industrial or municipal nutrient recovery operations which can help gain valuable products from waste water while simultaneously reducing pollution to wetlands.

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