A Novel Ion Exchange System to Purify Mixed ISS Waste Water Brines for Chemical Production and Enhanced Water Recovery

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Problem Statement

Current water recovery systems on ISS recover 70-90% of the water per cycle, with the remaining liquid trapped in a toxic brine stream

On the same token in order to provide food for astronauts for long duration missions plant growth for food production is needed, barring any breakthroughs in replicator technology

The main goal would be to somehow take the brine stream and convert it to plant nutrients and possibly water for recycle to "close the loop"

Possible Solution

Chlor-alkali is a electrochemical process that takes brine solutions (sodium/potassium chloride) and converts them to useful chemicals (acids/bases/bleach) using electricity at high amperage

Chlor-alkali cells sometimes use bipolar membrane cells using ion-selective membranes that are vulnerable to hardness fouling

If we combine chlor-alkali treatment with ion exchange pre-treatment to remove contaminants we should be able to utilize this established terrestrial technology

All the ion exchange resins can be regenerated using the products of chlor-alkali leaving a spent regenerate fluid that can be used as a plant fertilizer
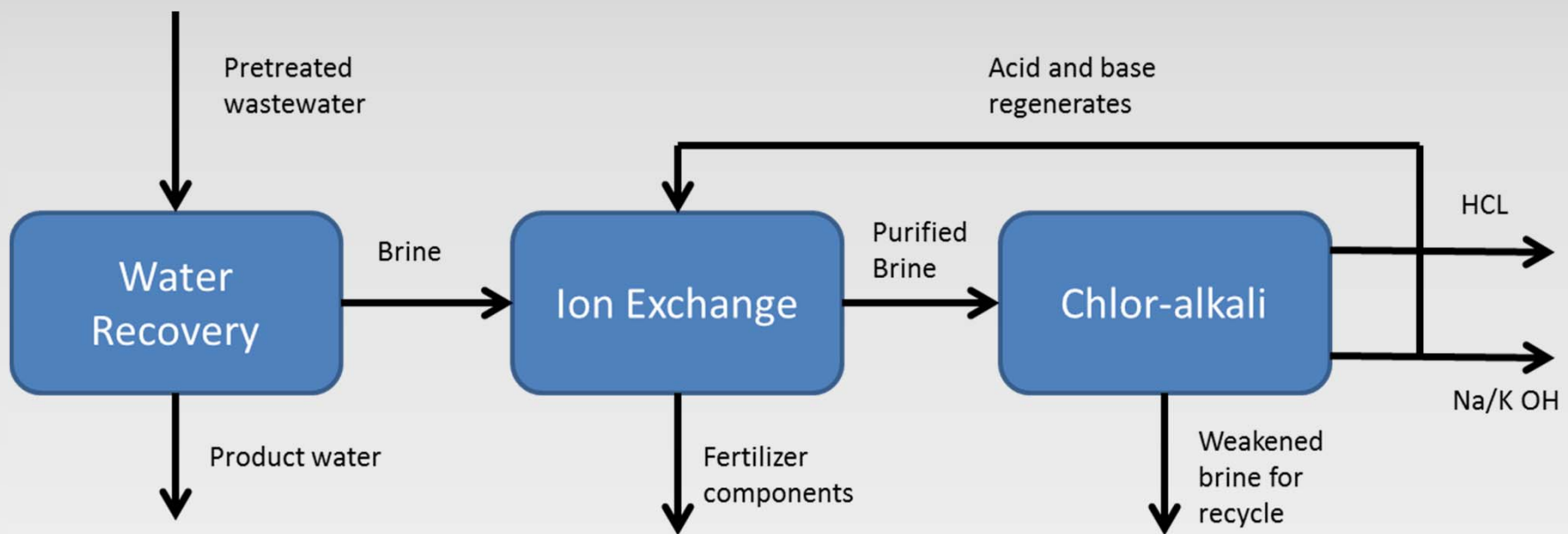
Basic Water Recovery Paradigm

Urea removal → Ammonia removal → Water recovery → Brine recovery

Water recovery → Water polishing
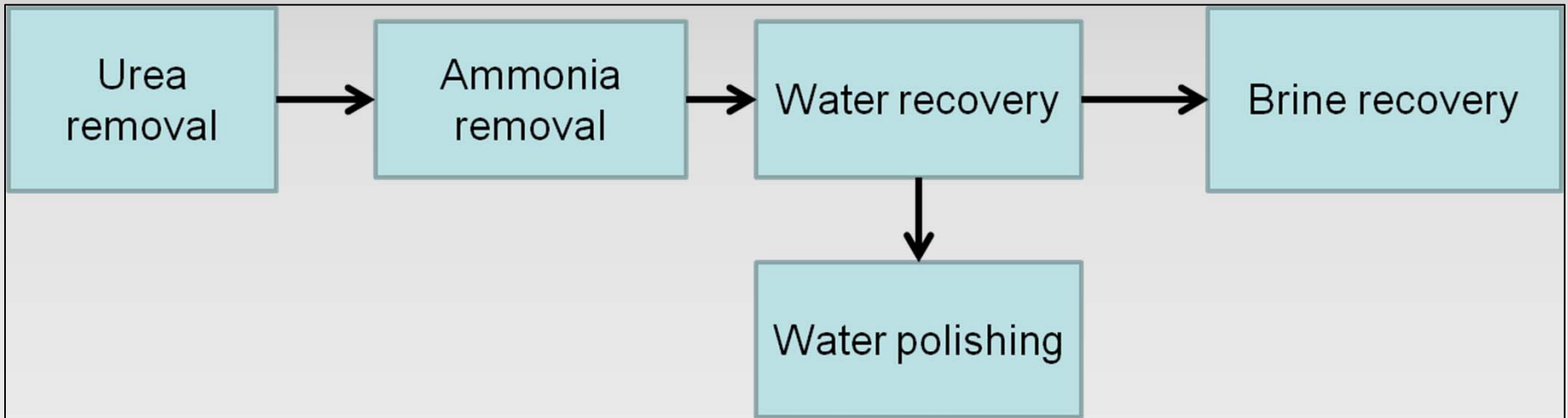
Brine Recovery in Detail

Ion Exchange Requirements

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 ions" (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.
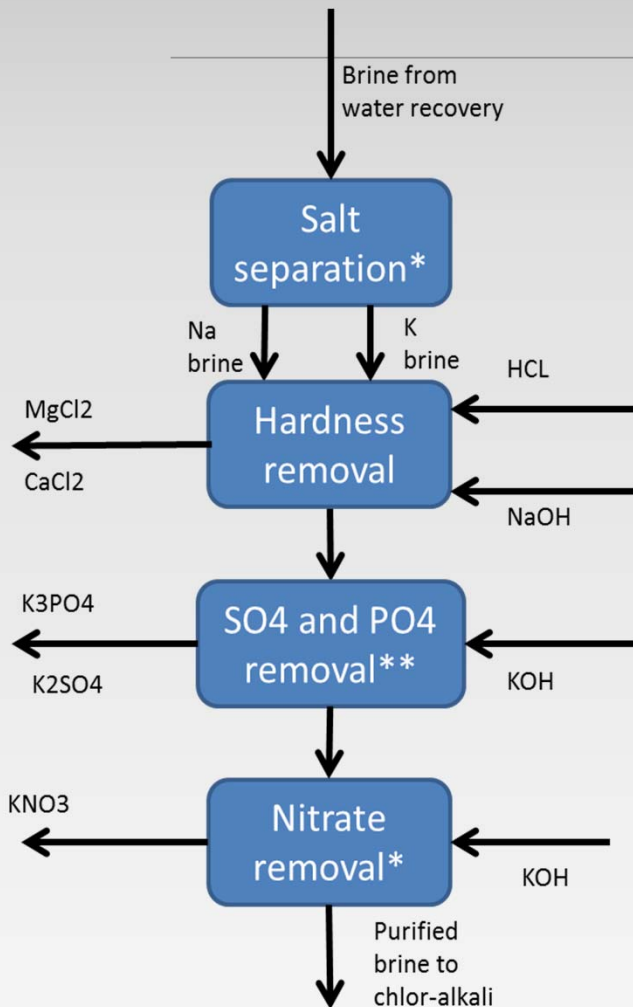
Candidate resins should have a high resistance to osmotic stress and survive potentially 1000's of duty cycles.

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 contaminates for the chlor-alkali processing (organic residues).

Preliminary Process Flow Diagram

Brine from
water recovery

Salt
separation*

Na
brine

K
brine

HCL

MgCl2

CaCl2

Hardness
removal

NaOH

K3PO4

K2SO4

SO4 and PO4
removal**

KOH

KNO3

Nitrate
removal*

KOH

Purified
brine to
chlor-alkali

*Our salt separation process uses either a dried brine and subsequent electrostatic separation into sodium and potassium components (proved at bench scale) or via electrically switched ion exchange using a porous electrode (used in pulp industry) on a wet brine. Without plant systems there would be no need to do this process

** Sulfate and Phosphate removal are not needed if plants are not utilized. The acid product would be mixed HCL/H2SO4/H3PO4

*** Nitrate removal is only needed with upstream nitrification. If ammonia makes it to the brine either dowex w50x8 would be used (a cation exchange resin) or KSC's proprietary struvite process to regeneratively remove and concentrate the ammonia stream for possible reuse (fertilizer or refrigeration)

Methods and Materials

Identify and create erzazt waste water brines of various water recovery % (90% and 95%) with various ions missing to simulate upstream treatments (as well as non-nitrifying systems)

Evaluate candidate resins using equilibrium study procedures established by Dow Chemical

Evaluate candidate resins using column study procedures established by Dow Chemical

Use Ion Chromatography (IC) and ICP-OES to develop mass balances and determine selectivity and capacity for the target ion.

Hardness Removal

Amberlite® IRA747 was chosen for its known ability to deharden brines and is already used in the chlor-alkali industry.
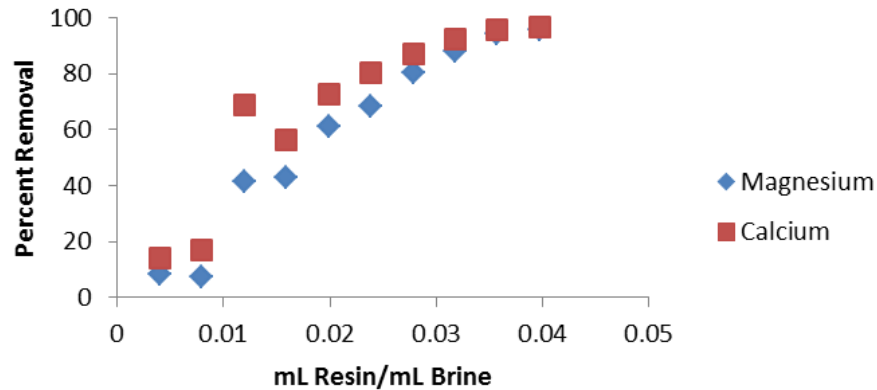
Performance on waste water brines was satisfactory with high capacity and selectivity at high relative flow rates.

Regeneration however is complex and high in consumable requirements.
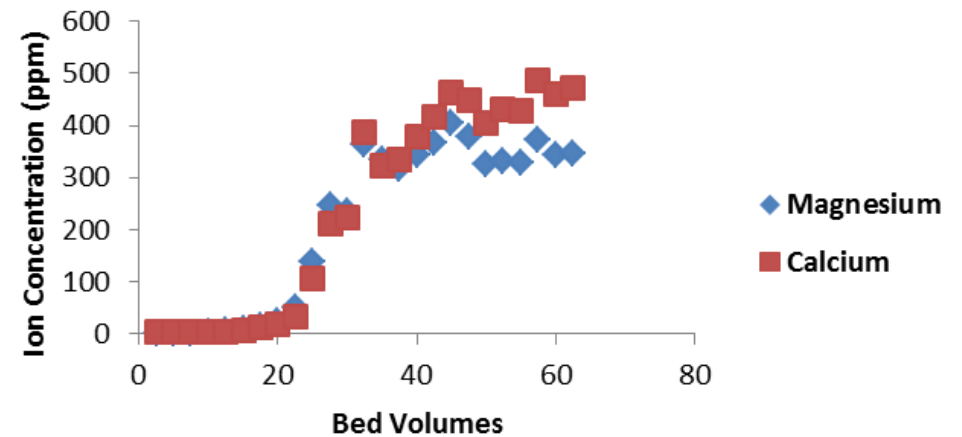
Hardness Removal Results

Hardness Removed as a Function of Treatment Ratio

Percent Removal vs mL Resin/mL Brine

- ◆ Magnesium
- ■ Calcium

Above estimates ~25:1 treatment ratio for our waste water brine simulate (at 90% water recovery)

Below Column tests confirm this

IRC747 Adsorption Run

Ion Concentration (ppm) vs Bed Volumes

- ◆ Magnesium
- ■ Calcium

Sulfate Removal

According to previous research, a zirconium modified M31 resin (M31z) has high capacity and selectivity for sulfate in brines. Unmodified M31 has no anion exchange capacity.
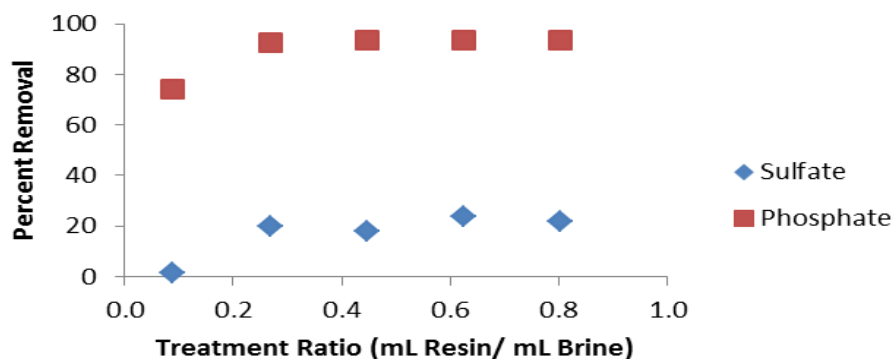
Data indicates that this is only true if phosphate is not present in the waste water, and pH is below 2 at very slow flow rates (<1BV/h at STP).

Selectivity and capacity for phosphate however is extremely good and better than the previously known state of the art. This seems to be a function of brine pH.
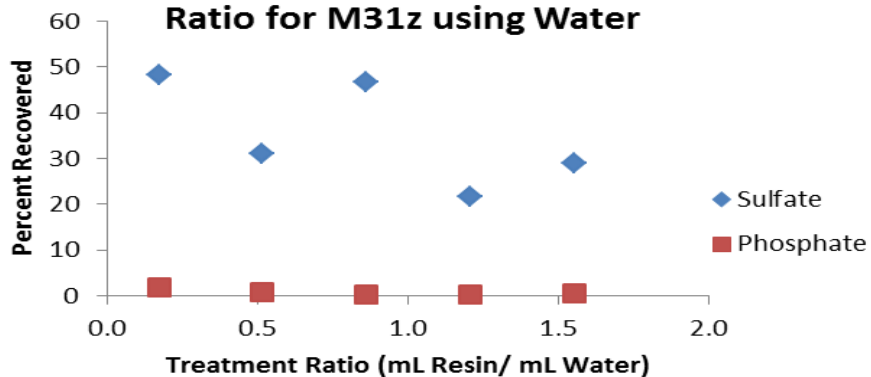
Sulfate Removal Results
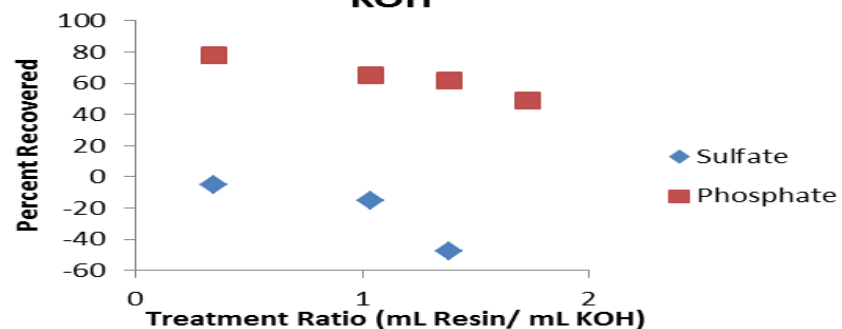
Left: M31z under acidic conditions removes phosphate

Corner: M31z regenerated with water only releases Phosphate

Bottom: M31z regenerated using caustic recovers a large fraction of Phosphate

Phosphate Removal

A commercially available phosphate resin for use in drinking water was tested to see if it would work in brine (Layne® RT and Layne® RT SW).
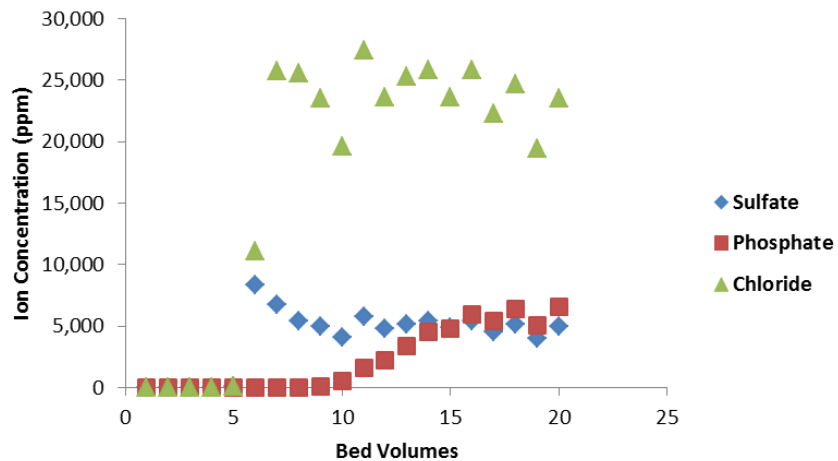
Selectivity was marginal with significant competition from chloride and sulfate.

Regeneration shows large sulfate desorption values that need more investigation.
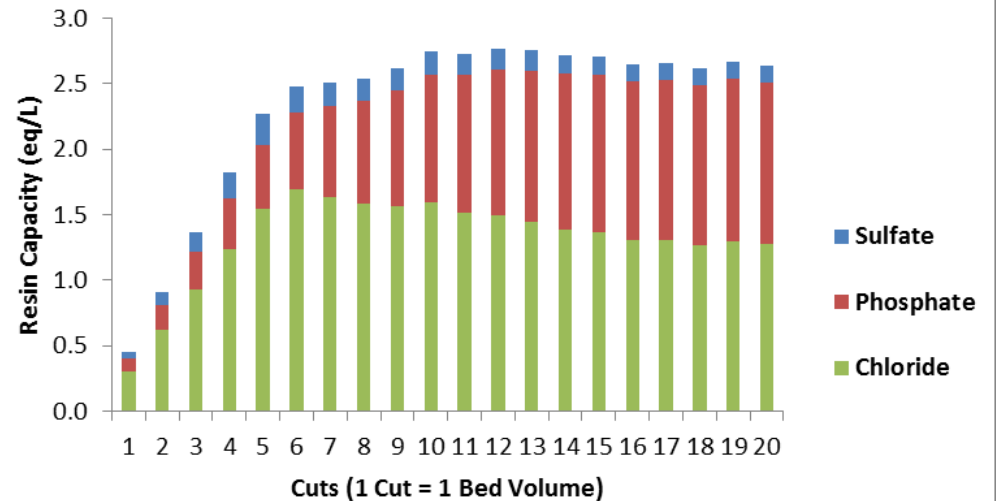
Phosphate Removal Results

Layne RTSW Adsorption Run

Above: Layne RTSW has decent breakthrough curve for phosphate

Below: However Resin selectivity leaves something to be desired

Layne RTSW Resin Selectivity Run

Nitrate Removal

Anion Exchange resins are normally more selective to nitrate than chloride, but this difference is relatively small.

Polyethyleneimine has been proposed as a modification to prevent chloride uptake and therefore increase the selectivity for nitrate over chloride.

After rigorous testing no difference was found between the modified and unmodified IRA 900 resin. Also column studies were worse in selectivity than the equilibrium studies.

More work needs to be done on the amounts of PEI used and to determine if a chromatographic regeneration can be performed to separate nitrate and chloride.
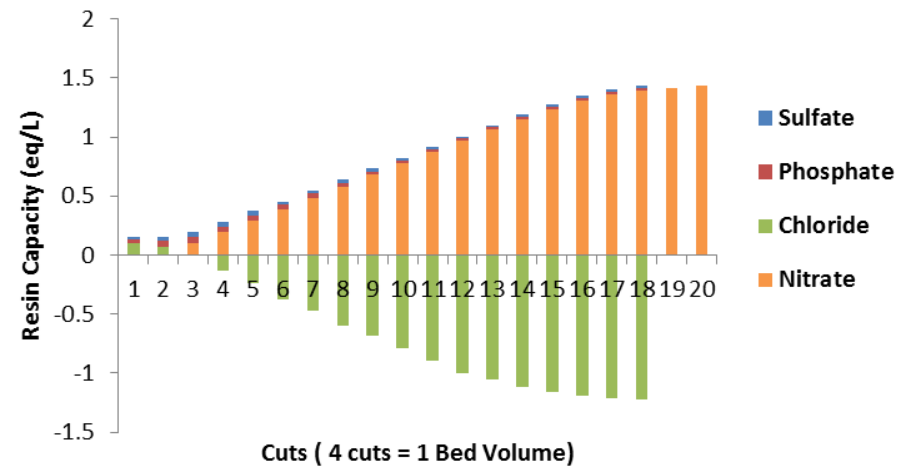
Nitrate Removal Results

IRA900 Adsorption Run
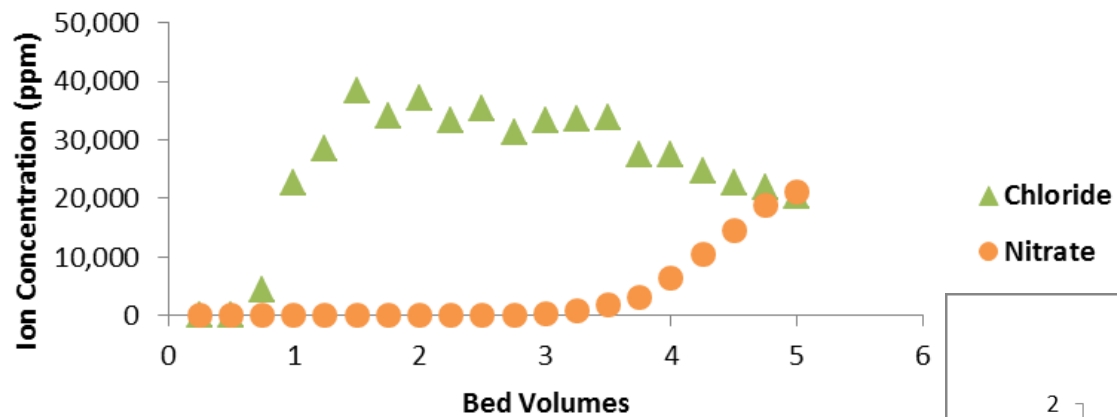
- ▲ Chloride
- ● Nitrate

Below: Selectivity was near unity when under hydroxyl-loaded resins (below example shows chloride dumping)

Above: IRA900 had decent kinetics for Nitrate when chloride-loaded (not practical for real systems)

IRA900 Resin Selectivity Run

- ■ Sulfate
- ■ Phosphate
- ■ Chloride
- ■ Nitrate

Cuts (4 cuts = 1 Bed Volume)

Summary Table of Performance

| Ion	Hardness	Sulfate	Phosphate	Nitrate
Resins	IRC747	M31z	M31z	IRA900PEI*
Selectivity	40:1 or better Ca:Na ratio	20:1 or better SO4:Cl with the absence of Po4 at low pH	20:1 or better Po4:Cl ratio	Slightly above unity NO3:Cl ratio
Capacity of target ion	Over 1.4 Eq/L	.4 Eq/L or better (needs more testing)	Over 1.5 Eq/L	Over 1.2 Eq/L
Expected BV ratio at 90% water recovery	Over 22.5 Bed Volumes	Over 10 Bed volumes expected	Over 10 Bed volumes	3 Bed volumes with current selectivity, goal is 5 bed volumes with enhanced selectivity

Updated Process Flow Diagram
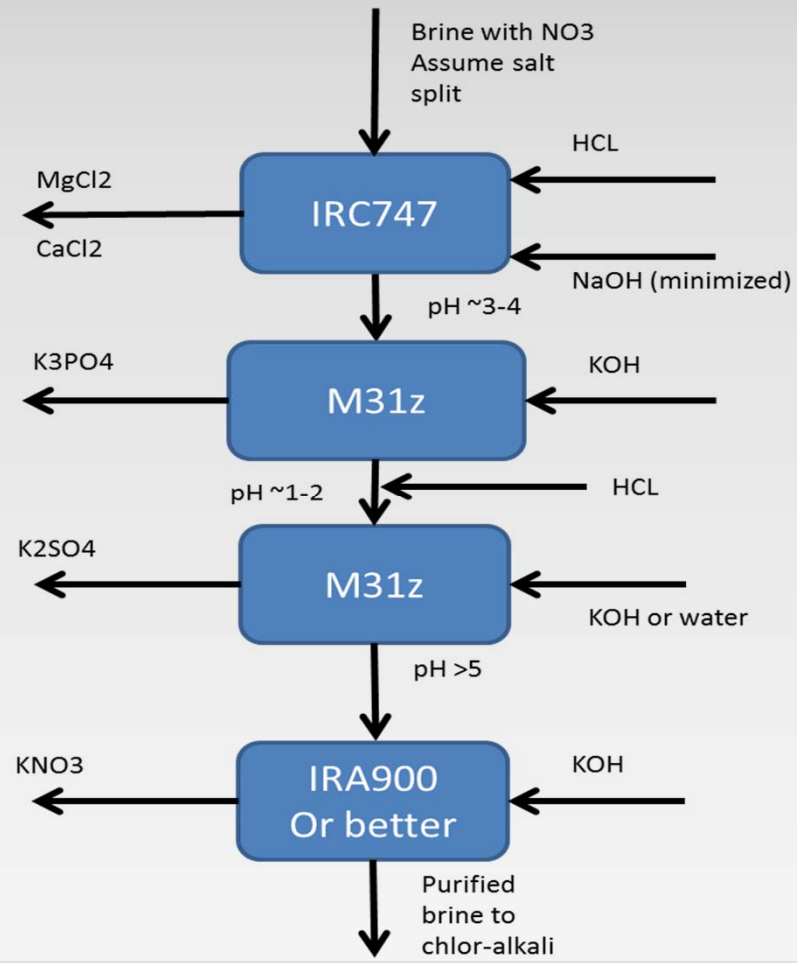
PFD with Upstream Ammonia Removal/Rejection
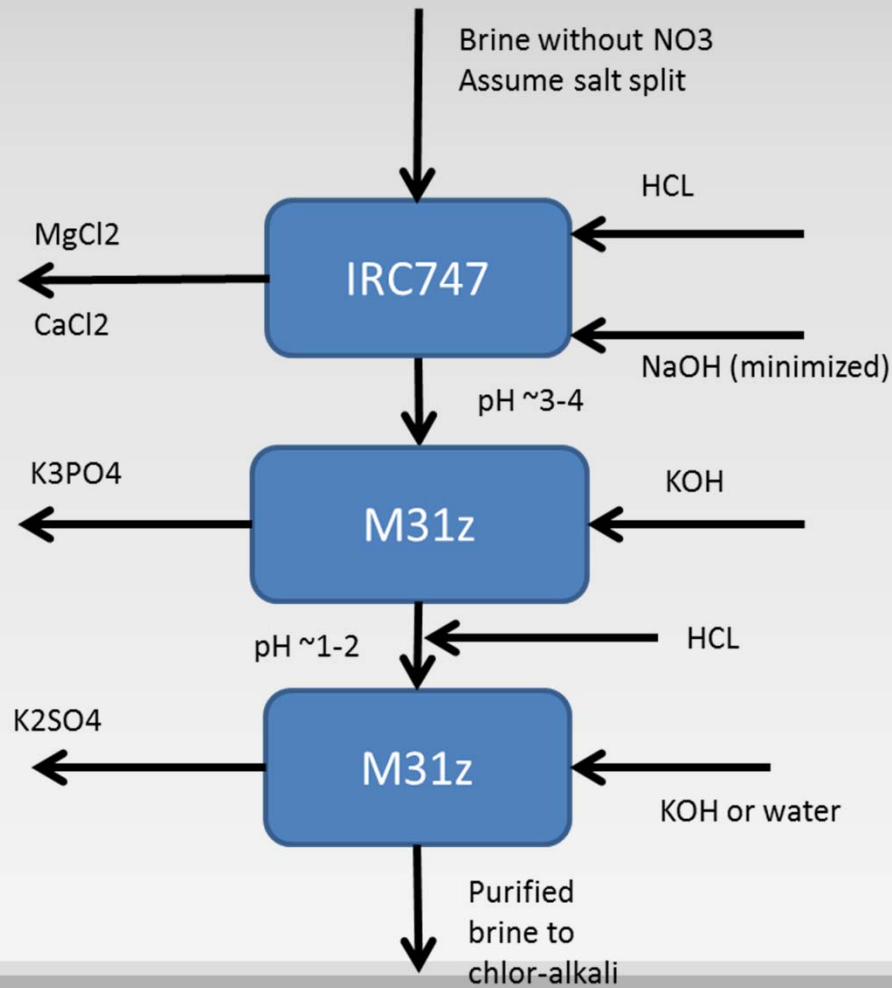
Recommendations

Most of the ion exchange technologies seem viable enough to attempt brine purification.

This has led us to 2 system architectures depending on upstream nitrogen type and with/without plant system integration for a potential staged approach.

Some issues with selectivity, capacity, and kinetics need to be addressed to minimize the regeneration requirement to allow the system to sustain off chlor-alkali products.

Regenerate recycling was not tested but will most likely allow the system to operate in a closed loop manner as long as sufficient "priming" products are brought up with it.

Future Plans

With procedures and methods established, more resins and resin modifications can be tested once they become available and/or discovered.

More equilibrium studies should be performed to determine adequate contact times and PH regimes for optimization.

Integration of all the ion exchange processes and downstream chlor alkali will be needed with the use of real waste water brines for short term and life cycle testing.

Further integration will be needed with the water recovery system and hydroponic systems to confirm that this "closed loop" system is viable.

Further Study M31z to better understand it's PH dependence and determine if it is commercialize-able

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