Flowsheet Validation for the Permanganate Digestion of

Reillex™ HPQ Anion Resin

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September 23, 2009

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Flowsheet Validation for the Permanganate

Digestion of Reillex™ HPQ Anion Resin

by

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Summary

The flowsheet for the digestion of Reillex™ HPQ was validated both under the traditional alkaline conditions and under strongly acidic conditions. Due to difficulty in performing a pH adjustment in the large tank where this flowsheet must be performed, the recommended digestion conditions were changed from pH 8-10 to 8 M HNO_3. Thus, no pH adjustment of the solution is required prior to performing the permanganate addition and digestion and the need to sample the digestion tank to confirm appropriate pH range for digestion may be avoided. Neutralization of the acidic digestion solution will be performed after completion of the resin digestion cycle. The amount of permanganate required for this type of resin (Reillex™ HPQ) was increased from 1 kg/L resin to 4 kg/L resin to reduce the amount of residual resin solids to a minimal amount (<5%). The length of digestion time at 70 °C remains unchanged at 15 hours. These parameters are not optimized but are expected to be adequate for the conditions. The flowsheet generates a significant amount of fine manganese dioxide (MnO_2) solids (1.71 kg/L resin) and involves the generation of a significant liquid volume due to the low solubility of permanganate. However, since only two batches of resin (40 L each) are expected to be digested, the total waste generated is limited.

Introduction

HB-Line Phase II has utilized multiple anion exchange columns for the purification and concentration of Np and Pu for the production of oxides. The recent Np campaign used two columns of Reillex™ HPQ anion exchange resin (each containing nominally 40 L of resin). The original disposal plan for this resin was to slurry it out of the columns with 8 M HNO_3 and transfer the resin and acid solution to H-Canyon Tank 5.2 where it would be neutralized with NaOH, treated with permanganate ($KMnO_4$) and heated to partially oxidize and solubilize the resin. The digested resin will be pH adjusted (pH ~14) and then sent to the Tank Farm. Fundamentally, this flowsheet involves oxidation of the solid organic polymer matrix to convert the polymer into aqueous soluble species and carbon dioxide (CO_2). The original intent of this dissolution process was to prevent localized high concentrations of carbonate caused by the deterioration of resin solids in the carbon steel tanks used to store wastes.
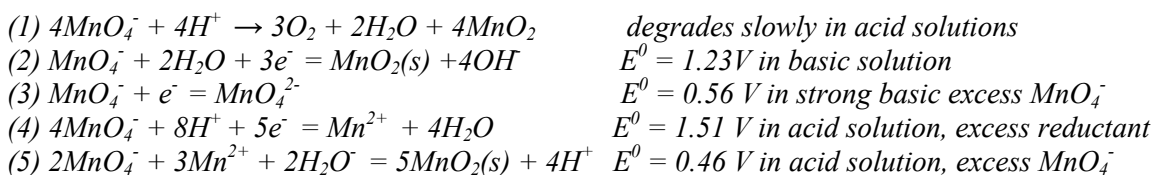
The purpose of the current work was to perform validation on the proposed resin digestion flowsheet per the request from H-Canyon Engineering.[1] The baseline flowsheet was based on work by Synder[2] where the feasibility of dissolving various ion exchange resins was shown. Significantly, the current request includes the need to compare against a Waste Acceptance Criteria (WAC) limit for ammonia (NH_3). Ammonium (NH_4^+) is present in various amounts in the chemicals used in H-Area and Reillex™ HPQ resin is composed of a polyvinyl-pyridine polymer. The nitrogen in the resin structure is a source of amines and NH_4^+/NH_3 during radiation or chemical induced decomposition. The final chemical state of either the NH_4^+/NH_3 from resin digestion was not determined in the past work[2,3,4,5]. The highly oxidizing flowsheet conditions may convert the NH_3 (or NH_4^+) to an oxidized species but this conversion was not established by the past work. Experiments in the current work were configured to capture the off-gas and measure for the presence of NH_3 (or NH_4^+). An NH_3 level of 1500 ppm has been proposed by H-Canyon[1] to meet the Waste Acceptance Criteria (WAC) limit. Due to the difficulties involved in adjusting the resin-HNO_3 mixture to the historical pH 8 to 10 target additional testing in acidic media up to molar concentrations of HNO_3 was added to the scope.

Baseline Digestion Flowsheet: The italicized paragraph below represents the H-Canyon proposed plan for performing the digestion of this resin.[1] The current work proposes modification of this plan to improve the completeness of digestion and to enable implementation in the plant equipment.

"HB-Line will transfer the resin from one column to Tank 5.2 using 8 M HNO_3 to float and flush the resin from the column. Additional 8 M HNO_3 will be transferred to Tank 5.2 to obtain 17 L of 8M HNO_3 per L of resin transferred. H-Canyon will add 50 wt % NaOH to Tank 5.2 to neutralize the acid and adjust the pH to a slightly alkaline condition (~pH 8) followed by a $KMnO_4$ addition of 1 kg of $KMnO_4$ per liter of resin. Tank 5.2 will then be agitated and heated to ~71 to 76 °C for 15 hr after which the tank will be cooled and a final 50 wt % NaOH adjustment to 1.2 M excess NaOH prior to transfer to the tank farm (without any sampling or solution analysis). H-Canyon does not intend to take normal process samples (utilizing the canyon sampler) from tank 5.2 due to expected pluggage from resin/MnO_2 solids." Sampling by "dip" method from the top of the tank would avoid this problem but would involve significant additional effort.

Flowsheet Chemistry: The basic chemistry of permanganate digestion of organics was described in a review article by Ladbury[6]. The basis for the resin digestion flowsheet was originally developed by Snyder[2] and over the years, various aspects of the digestion have been evaluated by others (Wehner[3] and Walker[4]). The flowsheet was originally proposed using alkaline conditions to avoid volatilization of ruthenium (Ru), but oxidation of organics with permanganate can also be performed under acidic conditions. Since Ru is not expected to be present in the HB-Line resins or H-Canyon tank, the restriction of the process to alkaline conditions does not appear necessary. Snyder[2] indicated that at a pH of about 13, the reaction rate decreased about 25 to 50% relative to the rate observed at pH 8. At 1 M NaOH the reaction rate was decreased further due to the production of manganate (MnO_4^{2-}) instead of manganese dioxide (MnO_2). The fundamental redox chemistry of permanganate (MnO_4^-) is described by the equations below as described by Cotton[7] and Ladbury[6]. Note that total permanganate requirements for oxidation will vary with the final oxidation state of manganese primarily between the II and IV oxidation state. Also note that the amount of MnO_2 solids produced will vary depending not only on the amount of permanganate but also on the pH at which the digestion is performed. When performed under alkaline conditions any CO_2 produced will be retained as carbonate but under acidic conditions (< pH 5) any CO_2 produced will be released as a gas. NH_3 produced under moderately alkaline conditions is expected to be partially retained but under acidic conditions NH_3 will be completely retained as NH_4^+. Under highly acidic conditions, production of HNO_2 will provide a reducing species that will reduce both MnO_4^- and MnO_2 to Mn^{2+}. The following reactions summarize the behavior as a function of acidic or basic conditions.

(1) $4MnO_4^- + 4H^+ \rightarrow 3O_2 + 2H_2O + 4MnO_2$ ⁣ ⁣ ⁣ *degrades slowly in acid solutions*
(2) $MnO_4^- + 2H_2O + 3e^- = MnO_2(s) + 4OH^-$ ⁣ ⁣ ⁣ *$E^0 = 1.23V$ in basic solution*
(3) $MnO_4^- + e^- = MnO_4^{2-}$ ⁣ ⁣ ⁣ *$E^0 = 0.56 V$ in strong basic excess MnO_4^-*
(4) $4MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ ⁣ ⁣ ⁣ *$E^0 = 1.51 V$ in acid solution, excess reductant*
(5) $2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2(s) + 4H^+$ ⁣ ⁣ ⁣ *$E^0 = 0.46 V$ in acid solution, excess MnO_4^-*

Experimental

Test Description: Researchers digested small samples of Reillex™ HPQ resin in a closed evaporation apparatus similar to that used in recent work[8]. Figures 1 and 2 include a sketch and photograph of the apparatus. Initially a solution matrix of resin, HNO_3, NaOH (or alternately $NaNO_3$) was prepared at similar concentrations to the proposed baseline flowsheet. The solution was adjusted to target pH and solid $KMnO_4$ and water were added to match the proposed plant conditions. Acid solution (1 M HNO_3) in a gas washing bottle was used as an off-gas scrubber to capture any NH_3 evolved during the digestion for future analysis. The digestion was performed at 70 °C for nominally 15 hours. After the digestion completed, the pH of the solution in the closed digestion vessel was adjusted with base to greater than pH 12 to release the soluble NH_3 for capture in the acidic off-gas scrubber. The digestion solution (still heated to 70 °C) was sparged with Ar for 60 min to obtain a reasonable efficiency for NH_3 recovery. Afterwards, a second pH adjustment with acid was performed to release the dissolved CO_2 which was measured by collection in the Tedlar™ gas bag via water displacement. The capture of the gases in these simple solution matrices reduces the analytical complexity of measuring total NH_3 produced. A final step where the acidified digestion solution is further treated with sodium nitrite ($NaNO_2$) was used to dissolve the MnO_2 solids and establish the amount of resin residue. The solution from the digestion was then filtered

and the resulting solids were measured after air drying to quantify the amount of resin solids that remained. The efficiency of capture and retention of ammonia and carbon dioxide was confirmed by digestion (without resin) of ammonium sulfate and sodium carbonate both with and without permanganate.

When acid digestion was performed, less NaOH was added (none in most cases) to neutralize the initial 8 M HNO_3. Because acidic digestions were performed at < pH 2, CO_2 was not retained by the digestion solution and it bubbled out through the scrubber during the digestion step. The CO_2 collection steps were not performed for acidic digestions. Also after acidic digestions the reduction of the MnO_2 to Mn^{2+} with $NaNO_2$ was performed prior to the recovery of NH_3.

Equipment: The experimental setup consisted of a 250 mL 4-port boiling flask fitted with a small condenser. Tygon® tubing (0.125 in. ID) connected a Swagelok® "T" at the top of the condenser to a gas washing bottle (scrubber) containing 100 mL of 1 M HNO_3 prepared with deionized water. The gas scrubber was carefully cleaned and rinsed prior to each experiment to avoid residual Na or NH_4^+ which would have affected the IC cation analysis. During the 15-h digestion phase of the experiment (typically performed overnight), the gas scrubber could either be left open to the atmosphere or connected to the gas collection. In most experiments the scrubber was left open to the atmosphere as gas did not appear to be collected during the initial digestions performed under basic conditions (pH 8-10).

The gas collection apparatus consisted of a 1-L Tedlar® gas bag that was submerged in a ~3-L glass kettle with a ~650-mL graduated cylinder installed on top.

Chemical Reagents: Reillex™ HPQ resin (Lot # 80302MA, Btl 15, 12/98) that had been obtained directly from the manufacturer was used in these experiments. Samples from this lot of resin had been previously used for the various ion exchange flowsheet studies for the Np project[9,10,11,12]. A sample of nitrate-form resin was filtered and air dried for to obtain a sample of dry resin that could be added by weight to the digestion experiments. This resin had a density of 0.644 g dry resin/cc.

Reagent grade $KMnO_4$ was used and added as a weighed dry chemical. The plant plans to use a 5.7 ± 0.2 wt % solution freshly prepared (<14 days old). In these experiments, dilution water was added after the $KMnO_4$ addition to keep the volume consistent with the plant plans.

Reagent grade anhydrous Na_2CO_3 and $(NH_4)_2SO_4$ were added as weighed dry chemicals in tests without resin as standards for CO_2 and NH_3.

Analytical Methods: The total amount of ammonia generated was determined by Ion Chromatography(IC) determination for cations (NH_4^+). Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) was used to measure residual organic carbon in the digestion solution after treatment with nitrite and filtration. Carbon released as CO_2 was calculated from the volume of gas generated when the digestion solution was acidified. A sample of the
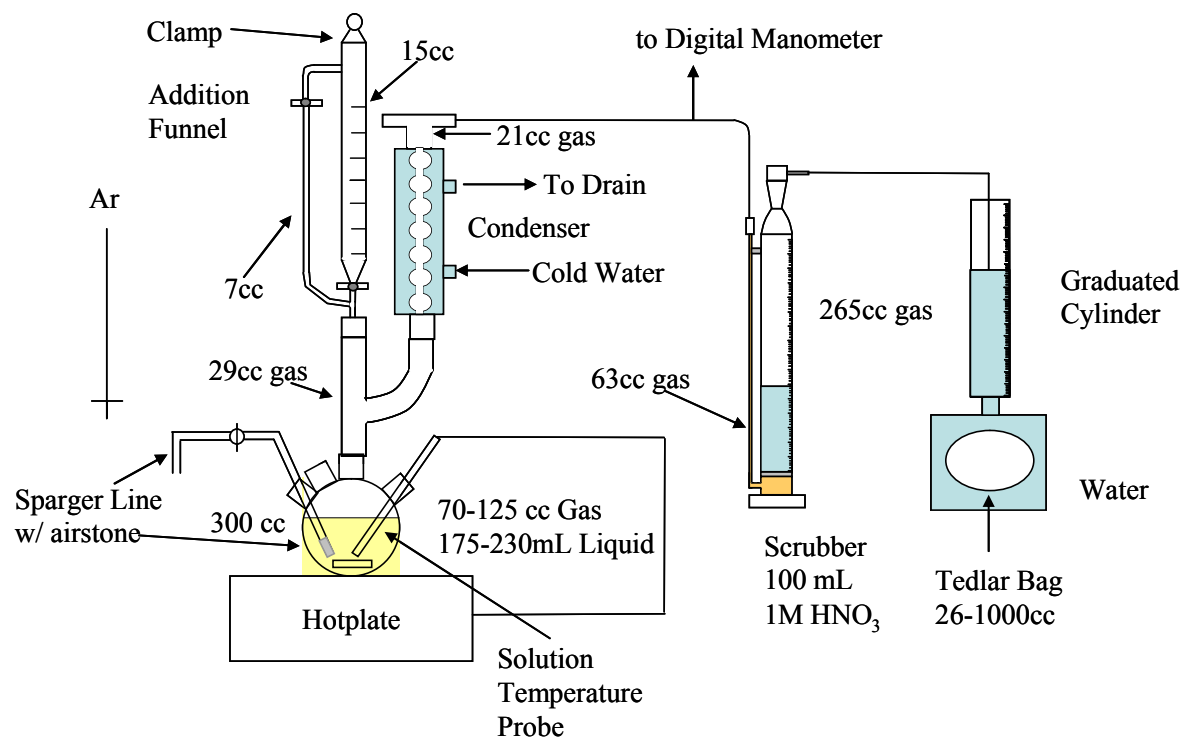
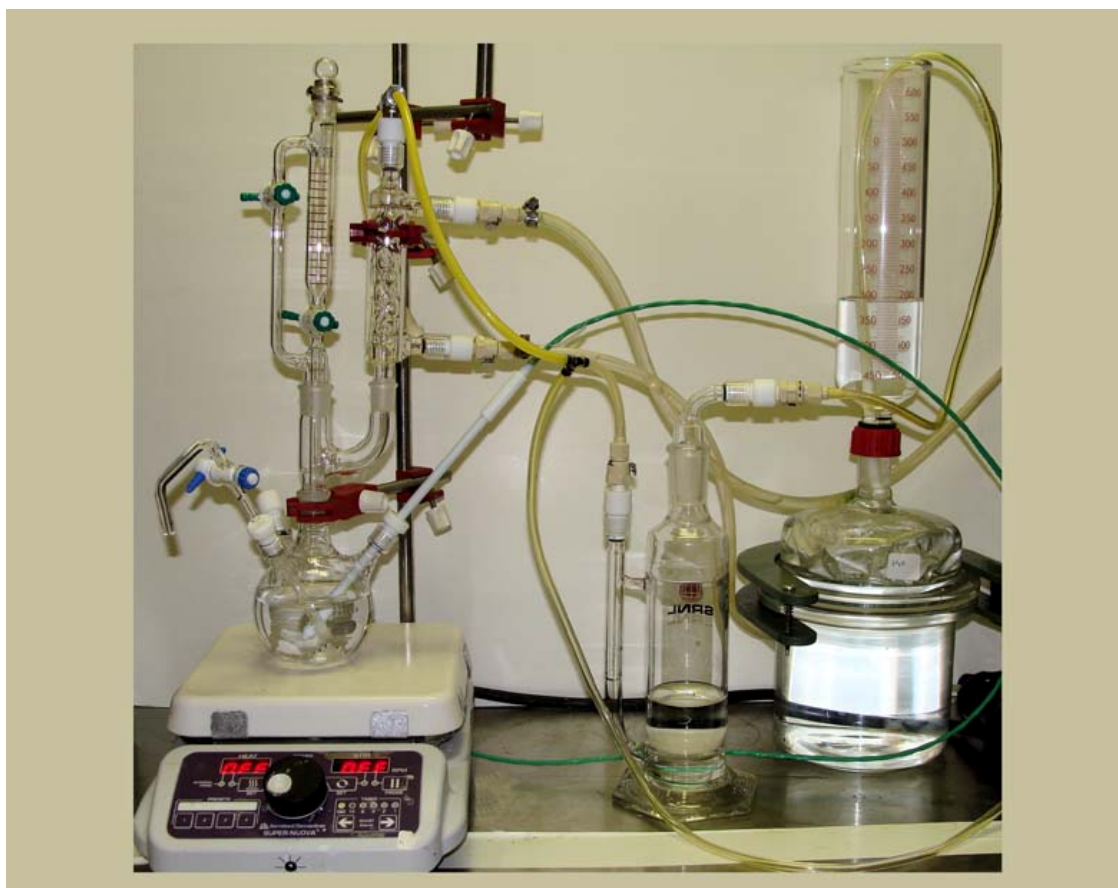Figure 1. Sketch of Experimental Apparatus Showing Typical Gas and Liquid Volumes.

Figure 2. Photo of Experimental Apparatus.

solids from an initial digestion batch was analyzed by Fourier Transform Infrared (FTIR) spectroscopy to identify the residue.

Samples for IC analyses were prepared by dilution with the mobile phase (30 mM methanesulfonic acid for cations) to within the calibration range (5-25 mg/L for cations). The Dionex® DX-500 Ion Chromatography system consisted of an AS-40 autosampler, a GP-40 gradient pump, and a CD-20 conductivity detector. Software control of the system and data acquisition was through Dionex® PeakNet 5.1. Columns and operating conditions are tabulated in the appendix.

The TIC/TOC analyses were performed utilizing an OI Analytical Model 1020A TOC Analyzer. This instrument measures total CO_2 via an IR detector. Organic carbon is initially oxidized in a furnace heated to 680 °C in an oxygen rich environment. The carbon dioxide is then swept quantitatively to the infrared cell and is selectively detected. Inorganic carbon must be released by acidification of the sample prior to measurement in a similar manner.

A Nexus 670 from Nicolet Instruments with an attenuated reflectance accessory was used to collect the FTIR spectrum of the Reillex™ beads and residue from initial resin digestion test using 1 kg $KMnO_4$/L resin. At a resolution of 4 cm^{-1} (wavenumbers) and a triangular apodization for reducing side lobes on adsorbing peaks, 200 scans were added to generate a spectrum with a signal to noise ratio of at least 300. All scans were conducted at room temperature. The instrument was calibrated using thin films of polyethylene issued from Nicolet Corporation.

Results

Permanganate Dose and Residual Resin Solids: The experimental conditions are tabulated in Table 1. Measurements taken during the experiments and analytical results are shown in Table 2. Initial testing was performed using the proposed rate of 1 kg $KMnO_4$/L resin. In the previous work by Walker[4], the author indicated that this ratio of $KMnO_4$ to resin would be sufficient to dissolve the resin leaving a significant amount of organic carbon in solution. In the current study, it quickly became apparent that a large amount of resin residue remained (based on visual observation) when digestion was performed at this ratio of $KMnO_4$ to resin. At a ratio of 3 kg/L resin, significant residue was still visible, but at 4 kg/L resin the amount of residue appeared minor by visual inspection. Dried residue weights and percentages calculated on an air-dried basis are listed in Table 2. The amount of resin used in the experiments, the weight of the filter paper and moisture levels in the solids limit the accuracy of the determination of residual solids below ~0.05 g (or ~4% of a 1.2 g resin sample). Note that in experiment "NH4 Resin Digestion 4kg-3", insoluble solids from the $NaNO_3$ biased the residual solids value high. Based on appearance, the resin solids appeared similar in amount to the previous test at 4 kg $KMnO_4$/L resin but other residue was also visible. Resin tests at 4 kg $KMnO_4$/L rate (pH 8-10 only) resulted in digestion solutions which remained purple colored after the digestion period (indicating that the solution still contained MnO_4^-). Unreacted permanganate was present even though small amounts of resin residue were still present after 16 to 18 hours of digestion. (Note that the variation in the digestion times was due to a combination factors including sparge cycles.)

Previously Walker[4] concluded that a 1 kg $KMnO_4$ /L resin rate would be appropriate for digesting this resin. However Walker did not dissolve the MnO_2 solids remaining after the reaction, but relied on TIC/TOC analyses of the solids to determine the amount of resin residue remaining after the digestion period. When Snyder[2] developed this method of resin disposal, success of the flowsheet was judged by the amount of the residue after the MnO_2 solids were

Table 1. Experimental Conditions for Resin Digestion Experiments and Control Tests.

		Resin	$KMnO_4$	Na_2CO_3	$(NH_4)_2SO_4$	Time	g $KMnO_4$
		cc	g	g	g	h	per L resin
1 kg/L digestion 5/5	pH 8-10	1.89	1.92	0	0	15	1.01
3 kg/L digestion 5/6	pH 8-10	1.86	5.76	0	0	16	3.09
1M HNO3 blank							
NH4 Trap Control 2	pH 8-10		0	2.99	0.50	1	
NH4 Trap Control 3	pH 8-10		0	0	0.50	1	
NH4 Trap Control 3b	pH 8-10		0	3.00	0.55	1	
NH4 Trap Oxidation 2	pH 8-10		7.58	3.02	0.57	18	~4
NH4 Resin Digestion 4kg	pH 8-10	1.87	7.62			17.5	4.07
NH4 Trap Oxidation 5	pH 8-10		7.63	3.00	0.53	17.8	~4
NH4 Resin Digestion 4kg-3	pH 8-10	1.89	7.66			17	4.06
NH4 Trap Control 5a	pH 8-10		0	3.04	0.53	1.5	
NH4 Trap Control 5b	pH 8-10		0	3.04	0.51	16.7	
Resin Digestion 4kg -8M	8M	1.88	7.61			16.7	4.05
Control 6 4kg-8M	8M		7.62		0.51	17.5	~4
Resin Digestion 4kg -pH2	pH 0-1	1.90	7.66			18.7	4.04
Control 6 4kg-pH2	pH 0-1		7.64		0.55	17.7	~4

Table 2. Results for Resin Digestion Experiments and Controls.

	Time	kg KMnO$_4$	CO$_2$	NH$_4$	TOC	Solids[2]		NH$_4$
	h	per L resin	cc[1]	ppm	ppm	g	%[3]	ppm[4]
1 kg/L digestion 5/5	15	1.01	na	na	na	0.75	62%	
3 kg/L digestion 5/6	16	3.09	390	na	na	0.16	13%	
1M HNO3 blank				2				
NH4 Trap Control 2	1		450	254				
NH4 Trap Control 3	1			349				
NH4 Trap Control 3b	1		415	343				
NH4 Trap Oxidation 2	18	~4	505	2				
NH4 Resin Digestion 4kg	17.5	4.07	50	32	399	0.03	2%	64
NH4 Trap Oxidation 5	17.8	~4	495	2				
NH4 Resin Digestion 4kg-3	17	4.06	490	9	338	0.11	9%[5]	19
NH4 Trap Control 5a	1.5		495	454				
NH4 Trap Control 5b	16.7		445	659				
Resin Digestion 4kg -8M	16.7	4.05	na	20	443	0.07	6%	39
Control 6 4kg-8M	17.5	~4	na	227				
Resin Digestion 4kg -pH2	18.7	4.04	na	4	234	0.11	9%	8
Control 6 4kg-pH2	17.7	~4	na	183				

[1]Gas volumes are reported under ambient conditions of ~25 °C and 1 atm.
[2]Air-dried solids after nitrite treatment to dissolve MnO$_2$ solids.
[3]Calculated as a percent of the initial dry resin weight.
[4]Maximum values for NH$_3$/NH$_4^+$ in digestion solution assume minimum recovery efficiency of 50%.
Note: Gray shaded values indicate less than the detection limit results.
[5]Value biased high due to NaNO$_3$ reagent solids. Actual resin solids appeared to be ~3%.

chemically dissolved with hydrogen peroxide. The current work relied primarily on dissolution of MnO$_2$ solids with nitrous acid (sodium nitrite in acid solution). Although the dissolution of MnO$_2$ does add additional complexity to the experiments, the additional effort provides a far more reliable result for determining the completeness of digestion over a chemical carbon analysis. A sample of the residue from the initial digestion experiment that used 1 kg KMnO$_4$/L resin was qualitatively analyzed by FTIR. The results of that residue were compared with a sample of as-received resin and showed oxidation of the resin structure.

Validation was only initially planned for a pH range of 8-10, but acid testing was added to widen the range of the flowsheet conditions for ease of implementation. Testing at 8 M HNO$_3$ did not involve neutralization prior to permanganate digestion and gave very similar results to those at pH 8-10. The amount of solid resin residue was 6%. When digestions were performed at pH 0-2 (partial neutralization) additional resin residue appeared to remain.

Material Balances: Control samples containing known amounts of (NH$_4$)$_2$SO$_4$ and Na$_2$CO$_3$ were used to verify the retention and recovery of NH$_3$ and CO$_2$. Table 3 contains the results of calculations for the total amount of NH$_3$ and CO$_2$ and the recovery for the control samples. Initial recoveries for NH$_4^+$ were very low (< 5%) and improvements in the equipment and technique were made to raise the recovery of NH$_4^+$. In those early trials (not reported here), low recoveries were observed that were attributed principally to insufficient volatility of NH$_3$ during sparging of the solution at ambient temperature. All data reported here used a 70 °C solution temperature and a minimum 1-hour sparge time. These improvements resulted in NH$_3$ recoveries from control solutions that were typically > 50%. Other improvements made

Table 3. Material Balances and Yield of CO_2 and NH_4^+.

	Observed		Theoretical				
	CO_2	NH_4	CO_2	NH_4	CO_2 [2]	NH_4 [2]	TOC
	mmol[1]	mmol	mmol	mmol			mmol
1 kg/L digestion 5/5							
3 kg/L digestion 5/6	16.5						
1M HNO3 blank							
NH4 Trap Control 2	19.1	2.82	28.2	7.52	67.7%	37.5%	
NH4 Trap Control 3		3.88		7.63		50.9%	
NH4 Trap Control 3b	17.6	3.81	28.3	8.25	62.1%	46.2%	
NH4 Trap Oxidation 2	21.4	0.03	28.5	8.57	75.1%	0.3%	
NH4 Resin Digestion 4kg	2.1[3]	0.41					7.7
NH4 Trap Oxidation 5	21.0	0.03	28.3	8.05	74.1%	0.3%	
NH4 Resin Digestion 4kg-3	20.8	0.11					6.1
NH4 Trap Control 5a	21.0	5.04	28.6	7.95	73.2%	63.5%	
NH4 Trap Control 5b	18.9	7.32	28.7	7.76	65.7%	94.4%	
Resin Digestion 4kg -8M		0.24					8.01
Control 6 4kg-8M		2.53		7.64		33.0%	
Resin Digestion 4kg -pH2		0.05					4.80
Control 6 4kg-pH2		2.03		8.34		24.4%	

[1]Calculated with assumption of gas collected at 25C and 0.5psig or 23.6 cc/mmol gas.
[2]Observed results calculated as a percent of theoretical.
[3]Observed amount of gas during addition of acid extremely low, cause not identified.

during the testing included converting the sparger over to an air stone (rather than just a ¼" glass tube) and using additional efforts to control glass joint leakage. For the latter half of the experiments (starting at the Digestion 4kg-3 and below in Table 1), Teflon™ rings and sleeves were placed on all ground glass joints and additional care was taken during assembly to test for leakage. The principal concern was that during the 15-hour digestion period, the small positive pressure on the system (< 2 inches water column) might allow significant ammonia to escape the system. In hindsight, the two most probable opportunities for incomplete recovery of NH_3 are incomplete volatilization from the digestion solution or incomplete capture by the scrubber solution. Note that the recovery of CO_2 in the control experiments was consistent in the range of 62 to 75% of the amount expected and did not appear to be affected by any of the changes.

MnO_2 Yield: Experiments that duplicated the digestion conditions at pH 8 to 10 and at 8 M HNO_3 were performed for the sole purpose of identifying the amount of MnO_2 produced by the digestion (see Table 4). These tests were duplicates of previous tests but no samples were analyzed and the MnO_2 reduction with $NaNO_2$ was not performed. Significant amounts of dark solids were formed but no resin residue was observed (based on the conditions, significant resin residue was not expected). The solids were filtered (without washing) and the

Table 4. Observed Total Solids Yield.

	Resin	KMnO4	Time	kg KMnO4	MnO_2[1]	Salts	Solids[2]		Solids
	cc	g	hr	per L resin	g	g	g		kg solids/L resin
Resin Digestion 4kg -8M	1.22	7.61	15.7	4.03	4.19	0.15	3.38	77%	1.71
NH4 Resin Digestion 4kg –pH8-10	1.20	7.61	15.7	4.08	4.18	1.39	5.29	93%	2.10

[1]Theoretical MnO_2 mass assuming 100% yield of MnO_2.
[2]Percent of theoretical MnO2 mass assuming insignificant contribution by residual resin mass (corrected for estimated salt content).

resulting cake was air dried and finally oven dried to 150 °C for several hours to a constant weight. A maximum mass of solids assuming no resin residue and 100% conversion of permanganate to MnO_2 was calculated. For the 8 M HNO_3 sample, the mass of solids equated to 77% of the possible MnO_2 solids, which when scaled by the amount of resin would equate to 1.71 kg solids/L resin. The sample digested at pH 8-10 produced significantly more solids than anticipated due to the soluble salts. After correction for the mass of Na and K salts, the remaining mass amounts to 93% of the possible MnO_2 solids or 2.10 kg solids/L resin. It was observed that the solids produced under alkaline conditions filtered more slowly and had a mud-like consistency after filtering, whereas the solids from the 8 M digestion filtered into a more "cake-like" structure. These observations suggest that the particle sizes may have been smaller for the alkaline digested solids however no analytical confirmation was attempted. Filtration behavior would also have been affected by the significant differences in solution properties. The solids produced from either experiment were easily suspended for transfer from the digestion container to the filter unit but these observations are not necessarily applicable to agitation conditions in H-Canyon.

NH_3/NH_4^+ Oxidation: Control oxidation experiments suggest that NH_3 was completely oxidized by the digestion process at pH 8-10 (see Tables 2 and 3). NH_3 was consistently reduced to non-detectable levels. However, resin digestion experiments at pH 8-10 consistently show small but detectable levels of NH_3. Under acidic conditions (both pH 0-1 and 8 M HNO_3), the resin digestion also resulted in small but detectable levels of NH_3 while the oxidative control samples showed that significant NH_3 remained in solution. The results suggest that only about half of the NH_3 was oxidized. Time did not permit the acidic experiments to be replicated. The results suggest that NH_3 in solution is readily oxidized under slightly alkaline conditions but that under acidic conditions NH_4^+ persists somewhat. The NH_3 values from the resin samples are small in all cases and it is not even certain that significant NH_3 yield from the resin structure should be expected. The resin tests consistently show much less than 50 ppm NH_3 produced. Assuming a minimum 50% recovery of NH_3 by the gas scrubber technique results in a maximum value of 64 ppm of NH_3 for the digested resin solution compared with the proposed WAC limit of 1500 ppm.

Reaction Rate: The nominal 15-h cycle time was established in the past work for alkaline resin digestion[2,3,4] No effort was made to optimize the digestion time and due to the heated sparge (for NH_3 recovery) that was routinely performed, most experiments actually remained heated for 17 to 18 hours. Digestions performed under highly-acidic conditions appear to react somewhat faster than those performed at pH 8-10. A single acidic experiment was performed where the gases evolved during the digestion were collected and monitored over time (see Table 5). Gas gently evolved without foaming (under acidic conditions, CO_2/CO is not soluble and is visible as small bubbles in the scrubber solution) during the initial 1 hour of the digestion. Only about half of the gas volume was collected as was observed in the comparable alkaline digestions. Possible causes for the reduced gas volume include the presence

Table 5. Short Time-Scale Acid Digestion.

		Resin	$KMnO_4$	Time	CO_2	kg $KMnO_4$		Solids[1]
		cc	g	h	cc	per L resin	g	
Resin Digestion 4kg -8M	8M	1.87	7.61	4.7	240	4.08	0.02	2%

[1]Air-dried solids after nitrite treatment to dissolve MnO_2 solids. Expressed as weight and as percent of initial dry resin weight.

of soluble organic carbon in the digestion solution (no TOC measurement was performed) or unusual gas leakage from the collection system (it passed the standard leak check). Conservatively assuming a total gas generation of 2x of that observed in 1 hour of the experiment results in a gas generation rate of 10.8 mmol of gas/min/cc resin. When scaled to a 40-liter batch of resin the volume becomes 436 moles of gas per hour or ~6 scfm compared to a typical offgas rate of 100 scfm for an H-Canyon vessel[13]. This digestion was halted after 4.7 hours; the MnO_2 solids dissolved by treatment with $NaNO_2$ and the resulting solution filtered. No solids were visible in the solution after the MnO_2 was dissolved but a very small amount of solids were collected by filtration. This result indicates that the reaction rate under strongly acidic conditions is significantly higher than the alkaline baseline case (pH 8-10).

Application: Resin digestion flowsheets have historically called for digestion under slightly alkaline conditions to avoid radioactive Ru volatilization which could cause a radioactive release to the environment[2]. However due to the age of the Np processed by the anion exchange resin (mostly recovered prior to 1985) and the relatively short-half lives of the Ru isotopes (~1 year) Ru releases are not a concern. Moreover, controlling the reagent additions to achieve the target pH of 8 to 10 prior to performing such a digestion is difficult in the existing equipment. A small excess of caustic would readily drive the pH over 13 which is reported to change the chemistry[2] and require an increase the amount of permanganate to solubilize the resin. The results from the current study show that resin digestion under highly-acidic conditions can be at least as effective as digestion at pH 8 to 10. The ratio of 4 kg of $KMnO_4$/L of resin that appears necessary for alkaline digestion probably could be reduced under highly-acidic conditions but no effort was made to determine an optimal level due to time constraints on this project.

Table 6 shows a volumetric breakdown for resin digestion with permanganate with the acid neutralization step delayed until after the digestion has been completed. Resin digestion at 4 kg $KMnO_4$/L resin with 5.7 wt % $KMnO_4$ results in the addition of over 70 L of permanganate solution per L resin. During the current study the production of 1.71 kg of MnO_2 solids per L of resin digested by this flowsheet was observed which equates to ~ 68 kg of MnO_2 per 4071 L batch (or 1.6 wt % solids). Past performance of alkaline resin digestion (with a dose of 1 $KMnO_4$/L resin) generated less MnO_2 solids but due to the smaller liquid volume appears to have generated ~1.3 wt% MnO_2 solids[3] as well as left another 0.7 wt % resin solids. Therefore the actual total solids loading of the solution produced by the proposed flowsheet is expected to be similar to that of past resin digestion.

Table 6. Volume Estimates for Proposed Acidic Resin Digestion Flowsheet.

	Vol, L	Total Vol, L	M	Mol	
Resin	40	40			
8M HNO_3	680	720	8	5440	17L acid/L resin
5.7 wt% $KMnO_4$	2807	3527	0.359	1006	4 kg $KMnO_4$/L [1]
		3527			Heat 71-76C for 15 hr
50 wt% NaOH	286	3813	19	5440	Adjust to pH 7
50 wt% NaOH	258	4071	19	4900	Adjust to 1.2M NaOH excess

[1]Assuming calculated density of 5.7% $KMnO_4$ solution to be 1.006 g/mL results in 70.2 L of 5.7% solution per L resin.

An alternative means of disposing of this resin as a solid waste is not available as the equipment was designed with resin digestion as the disposal path.

Recommendations

Digestion of Reillex™ HPQ anion exchange resin is recommended to be performed with 4 kg $KMnO_4$/L resin under acidic conditions. Digestion prior to neutralization of the HNO_3 with NaOH will allow digestion of the resin with limited organic residue (2-6 wt %) without the difficulty of adjusting to an intermediate pH level. A 15-hour digestion cycle is recommended based on past work. The amount of $KMnO_4$ and the length of digestion time have not been optimized but have been selected to ensure successful digestion.

Note that this process generates significant quantities of waste. Application in another facility should consider the alternative of removing the resin as a solid and directly disposing of the resin as a solid waste but that is not a practical option in the current situation.

Conclusions

Digestion of Reillex™ HPQ anion exchange resin has been successfully demonstrated under both slightly-alkaline and strongly-acidic conditions. Little resin residue remains after a 15-hour digestion at 70°C. A significant quantity of MnO_2 is generated from this digestion (1.71 kg per L resin) as well as a significant quantity of liquid volume due to the dilute permanganate concentration used. Very limited amounts of NH_3/NH_4^+ (8 to 64 ppm observed when calculated assuming 50% recovery) were observed to be generated during the digestion of this polyvinylpyridene resin. Under alkaline conditions permanganate appeared to oxidize greater than 99% of the ammonium added whereas under acid conditions ~ 50% of the ammonium added was oxidized.

Acknowledgements

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Appendix

Table 7. IC Cation Method Analytical Conditions.

Injection	20 μL
Flow rate	1.0 mL/min
Stop Time	15 min
Guard Column	IonPac CG-16 5x50 mm
Analytical Column	IonPac CS-16 5x250 mm
Suppressor	Self-Regenerating Suppressor (SRS) 300
Mobile Phase	30 mM Methanesulfonic acid
Calibration Curve	5 mg/L to 25 mg/L, $r^2 = 0.995$
Retention Times	NH_4^+ 7.5 min
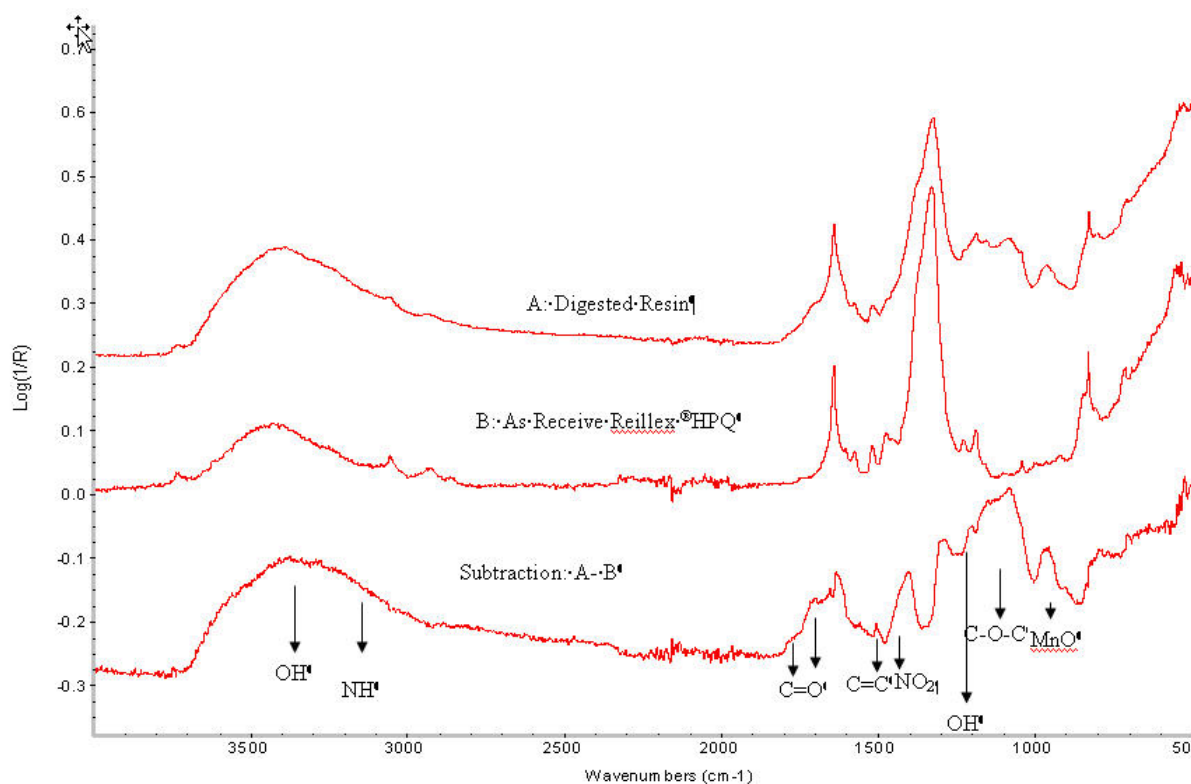
Figure 3. FTIR Comparison of Digested Resin Residue Compared with as-received Reillex™ HPQ Resin.