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Resins: Recommendation of
Denitration Processes*

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DENITRATION OF ROCKY FLATS ION-EXCHANGE RESINS: RECOMMENDATION OF DENITRATION PROCESSES

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by

Mary Barr, Wayne Smith, Jacob Espinoza

ABSTRACT

Resin denitration via anion-exchange is an implementable process that can effectively mitigate the hazards associated with stored resins in which the bulk of the nitrate consists of an "exchangeable nitrate" ionically bound to the cationic sites of the anion-exchange resins. Salicylate has been selected as the exchange anion of choice because of its superior selectivity for the Rocky Flats resins and its unique potential for comprehensive recovery and recycle. This report outlines a single recommended resin denitration procedure that is reasonably independent of the resin composition and the current stored form. This procedure is not optimized but rather seeks to 'over-treat' the resins so that a single procedure works for the variety of stored resins. The recommended treatment with sodium salicylate reduces resins by 95-99+% the measured exothermic behavior of the ion-exchange.

The explosive/fire hazard of nitrated resins has been long recognized as a problem for actinide processing. Recommended operating parameters for Pu processing are based, in part, on studies conducted in the mid-sixties that examined the thermal stability of nitrated resins in different configurations and chemical environments. The most spectacular 'mishaps' involving uncontrolled thermal reactions of resins occurred in the presence of substantial amounts of excess nitrate (as either nitric acid or plutonium hexanitrate). Stored ion-exchange resins at Rocky Flats have been rinsed with water, thus reducing, but not eliminating, the potential for uncontrolled exothermic reactions. Certainly the focus so far has been the determination of safe processing conditions rather than safe storage criteria.

Ion-exchange is a simple procedure that removes exchangeable nitrate from spent ion-exchange resin materials. Nitrate may exist on resins in three different chemical forms:

- 1) "Exchangeable nitrate" is ionically bound to the cationic sites of the anion-exchange resins. This nitrate may be as NO_3^- or as a complex anion such as $[\text{Pu}(\text{NO}_3)_6]^{2-}$. The term 'nitrated resin' is used herein to describe resins in which the exchangeable anion is nitrate.
- 2) "Excess nitrate" that resides in the aqueous matrix of the wet resin. This nitrate is easily flushed with deionized water and occurs in both the anion- and cation-exchange resins in which the resin was not completely rinsed with water prior to storage.
- 3) "Fixed nitrate" has been covalently bound to the resin material or otherwise immobilized through co-precipitation, reduction, etc. Nitration reactions occur extremely slowly in the absence of concentrated nitric/sulfuric acids and high temperatures. Covalently-bound nitrate is a minor portion of the total nitrate, and removal of fixed nitrate is not addressed by the denitration process recommendations.

This report outlines a single recommended resin denitration procedure that is reasonably independent of the resin composition (anion or mixed-bed) and the current stored form (rinsed or not, wet or dry, various amounts of Pu). This procedure is not optimized but rather seeks to over-treat the resins so that a single procedure works for the variety of Rocky Flats resins. Even major modifications to the general procedure (i.e., changing from column to batch processing) may still allow for comprehensive "bullet-proof" denitration of spent resins with relatively minor adjustments.

INTRODUCTION AND BACKGROUND

The yardstick for success in denitrating the resins is a sizable reduction (90–95%) in the exothermicity of the resins. Exothermicity is a measure of how much energy a material can spontaneously release at a certain temperature. For the ion-exchange resins, this energy is a function of the interaction between the oxidant (nitrate) and the substrate fuel (resin and/or any organic compounds). Determining the potential of a material to self-detonate or auto-combust requires comprehensive analyses of the onset temperature and magnitude of the exothermic reaction, as well as the rate of reaction and a multitude of other tests (shock sensitivity, time to ignition, etc.). These analyses and their interpretation are beyond the scope of this project. Fortunately, a simple examination of the magnitude of the exothermic reactions and their corresponding onset temperatures for the nitrated resins shows that the hazard associated with these resins is substantially reduced upon denitration by sodium salicylate. DSC (differential scanning calorimetry) provides the most accurate and important information concerning the initial and final "exothermicity" of the resins.

Selection of Denitration Anion

The desirable characteristics for the denitration of Rocky Flats' resins are as follows. Namely, the procedure must be simple, quickly implemented, and generate a minimum amount of RCRA-regulated and Pu-containing solutions. In fact, minimization of *all* wastes (aqueous and solid) is essential. No guidelines concerning the composition of the final resin form were presented, so a goal of 90-99% nitrate removal was established by the investigators at Los Alamos.

Based on the listed criteria, salicylate (2-hydroxybenzoate) was selected as the most probable anion for nitrate displacement from anion-exchange and mixed-bed resins. Five desirable properties of salicylate are listed below.

- 1) It has a very high selectivity coefficient for the resins used at RFETS. Table 1 summarizes the selectivity coefficients of various anions (relative to the hydroxide ion) for Type I anion-exchange resins (such as Dowex 11). Organic anions, particularly those with aromatic components, exhibit far greater affinity for the resins than do inorganic anions. Therefore, denitration occurs with smaller amounts of displacing anion minimizing both solution and solid wastes.
- 2) It has a very low affinity for Ca^{2+} and Mg^{2+} . If cementation of the final waste form is preferred, then the low affinity for calcium is advantageous. Salicylate's low affinity (relative to hydroxide) for M(IV) and M(VI) suggests that plutonium elution caused by complexation should be minimal under the near neutral pH conditions of 2 M sodium salicylate (pH ca. 6).

Table 1. Selectivity Coefficients and Ion Affinity Data

Ion	K_d^a	$\text{p}K_a$	$\log K \text{ M(II)}^b$	$\log K \text{ M(IV)}^b$	$\log K \text{ M(VI)}^b$
Salicylate $\text{L}=(2\text{-HOC}_6\text{H}_4\text{CO}_2)^{-1}$	450	2.8	0.66 (Ca)	4.3 (Th)	2.2 (U)
Citrate $\text{L}=[\text{HOC}(\text{CH}_2\text{CO}_2)_2\text{CO}_2]^{-3}$	220	5.7	3.5 (Ca)		7.4 (U)
Hydrogen Sulfate $\text{L}=(\text{HSO}_4)^{-1}$	85	1.6	1.5 (Ca)	3.7 (Pu)	2.2 (Pu)
Nitrate $\text{L}=(\text{NO}_3)^{-1}$	65		-0.2 (Ca)	0.5 (Pu)	-0.3 (U)
Chloride $\text{L}=\text{Cl}^{-1}$	22		0.2 (Ca)	-0.1 (Pu)	0.1 (Pu)
Acetate $\text{L}=(\text{CH}_3\text{CO}_2)^{-1}$	3.2	4.6	0.6 (Ca)	3.9 (Th)	2.2 (Pu)
Hydroxide $\text{L}=(\text{OH})^{-1}$	1		1.0 (Ca)	12.1 (Pu)	7.6 (Pu)

^a Selectivity Coefficients courtesy (K_d) of Dow Chemical Co.

^b $\log K$ for $\text{M} + \text{L} \leftrightarrow \text{ML}$ from NIST Critical Stability Constants of Metal Complexes Database (#46), 1993.

- 3) Salicylate is readily precipitated from water as salicylic acid. Precipitation reduces the concentration of salicylate in the aqueous waste stream by 99+%, and the salicylic acid may be recycled for use in other denitration experiments. Colorimetric assay using Fe^{3+} provides a simple, effective procedure for quantification of excess salicylate in the aqueous wash. No other inexpensive anion (organic or inorganic) is so easily recovered or so amenable to assay.
- 4) The salicylate anions can be destroyed along with the resins by using any organic destruction process such as combustion, pyrolysis, or hydrothermal processing. Inorganic anions would leave solid residues.

- 5) Salicylate is not a RCRA-listed organic material. It is used extensively in the pharmaceutical and food industries and is commercially available in large quantities. It should meet with public acceptance.

EXPERIMENTAL AND RESULTS

Analytical Procedures

An MS Excel™ spreadsheet was developed to calculate the expected percent exchange based on log K selectivity values provided by Dow (Table 1). Dowex 11 (chloride form) was nitrated using 2 M HNO₃ in either repetitive batch mode or column mode using amounts calculated to yield better than 99.5% exchange. Equilibrium equations are given in Appendix 1. Percent nitrate and salicylate values reported below are based on the number of ion-exchange sites, not mass. Analyses (CHN analyses and salicylate uptake) of the nitrated resins suggest that air-dried resins have nearly twice their "as-purchased" capacity, probably due to loss of excess moisture.

While nitrate concentrations in solution may be measured using a nitrate-selective electrode, this procedure is of limited practical use because even low levels (0.001 M) of salicylate interfere with accurate nitrate readings. Determination of residual nitrate levels on the ion-exchange resins is similarly problematic with the high levels of salicylate "swamping" the spectroscopic signals (ultraviolet and infrared) of nitrate. Therefore, all stated nitrate concentrations are estimates based on the average capacity of the resins and their mixtures.

Salicylate concentrations of certain effluent solutions were determined spectrophotometrically using a commercial assay kit. Concentrations from 10⁻⁵ to 10⁻³ M may be accurately assayed. More concentrated solutions must be diluted prior to analysis. The procedure is outlined in Appendix 1. 2.0 M solutions of sodium salicylate were used in the denitration experiments. Lower concentrations generate larger volumes of aqueous waste and higher concentrations are difficult to make and are rather viscous. A 2.0 M solution is almost 1/3 sodium salicylate (by weight).

DSC measurements were acquired on a Perkin-Elmer 3700 DTA/DSC instrument at the standard rate of 10 degree/minute temperature ramp. "Cold" and "hot" samples were run on similar instruments located at the TA-55 and CMR complexes at Los Alamos, respectively.

DSC Data interpretation

In differential scanning calorimetry (DSC), the sample and a reference substance are subjected to a continuously increasing temperature. Heat is added to the sample (endothermic) or to the reference (exothermic) as needed to maintain the two at identical temperatures. The "onset temperature" of a reaction is derived by extrapolating the gaussian section of the curve back to a baseline.

The polystyrene substrate and functional groups of the anion- and cation-exchange resins undergo several endothermic reactions between room temperature and 500°C. For the as-purchased chloride form of Dowex 11, the major endotherm is centered around 100°C and is associated with the loss of excess water (Fig. 1). A second endotherm is centered around 260–270°C and is ca. 60 cal/g resin. A third exotherm of 30 cal/g is centered at 410–425°C.

Figure 1. DSC of Dowex resins. Endothermic reactions produce negative inflections and exothermic reacts produce positive inflections.

Quantitative displacement of the chloride by salicylate has very little impact upon the DSC beyond the expected fluctuations in the size of the water endotherm

The exotherm of the nitrated resin (ca. 180 cal/g resin at 300°C for the fully nitrated form) is superimposed upon the second endotherm of the resin substrate and makes it difficult to determine accurately the exothermicities of the nitrated/denitrated samples (Fig. 1). The establishment of a baseline for the calculation of the integrated peak areas for the small (>30 cal/g) exothermic peaks is a substantial source of uncertainty in the stated values. In general, the “best guess” at the baseline and integrated areas over-estimate, rather than under-estimate, the exothermicity of the final product. TGA of the fully nitrated resins indicate that the region of exothermic behavior consists of a complex mixture of reactions as is expected for rapid oxidation of the resin substrate (Fig. 2).

Samples that contain appreciable amounts of both salicylate and nitrate exhibit two discrete exotherms at approximately 320°C and 360°C (1C, Fig. 3 below). The two exotherms suggest that salicylate may act as an alternative fuel source for the nitrate. The sum of the areas is used to determine the total exothermicity (presented in the tables below). Resin with inorganic (chloride or hydroxide) anions exhibit a “threshold” behavior in which concentrations of nitrate below a certain level (ca. 10%) exhibit no detectable exothermic behavior. Salicylated resins do not appear to have such a threshold nitrate value.

Figure 2. TGA analysis of fully nitrated Dowex 11 anion-exchange resin.

Batch Experiments

The results of two small-scale batch experiments with Dowex 11 are given below. Each sample of fully nitrated resin (ca. 1.5 g) was placed in a plastic scintillation vial and allowed to contact with an equivalent volume of 2.0 M sodium salicylate (1 mL solution per 1 g of resin). Experiment B used a contact time of ca. 3 minutes, Experiment C used 10-minute contact times. After each contact, old solutions were drained off and new solutions were added. Samples 1B and 1C were allowed one contact, 2B and 2C two contacts, etc. The resins were rinsed twice with one volume of DI water (1 mL per 1 g of resin) after the final contact. "Calculated" percents salicylate and nitrate are based on the selectivity coefficients provided by Dow Chemical for Type 1 resins and the average measured capacity for the nitrated Dowex 11 resins (2.2 meq/g) using the equations in Appendix 1. Table 2 lists the batch denitration experimental results.

Table 2. Batch Denitration Experimental Results

Sample ID	calculated % salicylate	calculated % nitrate	exothermicity cal/g (B,C)	onset temp °C (B,C)
nitrated resin 5B, 5C (untreated)	0	100	139, 191	260, 262
1B, 1C (one contact)	68.9	31.1	79, 64	308, 293
2B, 2C (two contacts)	94.6	5.4	50, 33	340, 336
3B, 3C (three contacts)	99.2	0.8	19, 16	324, 326
4B, 4C (four contacts)	99.9	0.1	18, 17	308, 306

The samples in the C experiment consistently exhibit slightly lower exothermicities (in cal/g) than analogous samples in the B experiment. This suggests that longer contact times are more effective at removing nitrate. Total exothermicity correlates only qualitatively with the calculated nitrate concentrations. Additionally, the data exhibit a rapid leveling off of exothermicity relative to the calculated nitrate levels at ca. 10% of their original values. The exothermic reactions of the denitrated resins occur at higher onset temperatures compared to the fully nitrated forms, thus suggesting an improved margin of safety for storage of partially denitrated resins. DSC curves for samples 1–5C are presented in Fig. 3.

Figure 3. DSC data for Experiment C (batch contacts, 10 minutes).

“Cold” Column Experiments

Experiment D: Three small diameter columns (ca. 3/4") were loaded with ca. 5 g of nitrated Dowex 11 resin in DI water. These columns were eluted with one, two, and three volumes (1 mL solution per 1 g resin) of 2.0 M sodium salicylate, respectively, followed by a final rinse with 2 volumes of DI water. Solutions were eluted at a rate of approximately 3 minutes per volume (about 5 mL). The effluents and the rinse solutions were collected for salicylate analyses. The “determined” amount of salicylate on the resins was established from the difference between the amount of salicylate added to the resins and the amount eluted. Assuming that contact with three volumes of salicylate produces near quantitative displacement of nitrate (thus 100% salicylate

for sample 3D), the millimoles of salicylate retained by samples 1D and 2D were then used to calculate the percent of anion-exchange sites occupied by salicylate. Exothermicity data are presented in Table 3.

Table 3. Experiment D Data

Sample ID	determined % salicylate/nitrate	exothermicity cal/g, % of original	onset temp °C
fully nitrated resin	0 / 100	176, 100%	251
1D (one volume)	72 / 28	18, 10%	281
2D (two volumes)	89 / 11	14, 8%	282
3D (three volumes)	100 / 0	5, <3%	287

The greater effectiveness of column vs. batch mode is readily apparent from the dramatic decrease in exothermicity with just a single volume of salicylate. With exposure to a single column volume of salicylate, the exothermicity decreased by ca. 90% (1D). With three-column volumes, the observed exothermicity is less than 3% of its original value. A second column run under similar conditions exhibited no detectable exothermic behavior. The observed exothermicity does not correlate well with either the calculated or experimentally determined nitrate loading levels.

Experiment E: Four 5-g samples of (1) fully nitrated Dowex 11, (2) a 20/80 (1g:4g) mixture of Dowex 50W-x8 cation- and nitrated Dowex 11 anion-exchange resins, (3) a 50/50 (2.5:2.5 g) mixture of Dowex 50Wx8 and nitrated Dowex 11, and (4) Dowex 50Wx8 were loaded into small-diameter columns in DI water. Each column was eluted with 5 mL of 2 M nitric acid followed by DI water until the effluent tested neutral. Resin samples were treated with 1 M NaOH until basic (see Resin Neutralization Step below) then eluted with 3 column volumes (1 mL per g of resin) of 2.0 M sodium salicylate followed by a final rinse with 2 volumes of DI water. Solutions were eluted at a rate of approximately 3 minutes per column volume (about 5 mL). The effluents and the rinse solutions were collected for salicylate analyses. DSC measurements were conducted on each batch of resin in its fully nitrated starting form and in its final “denitrated” state. Exothermicity data are presented in Table 4.

Table 4. Experiment E Data

Sample ID	cal/g nitrated	onset temp °C nitrated	cal/g denitrated	onset temp °C denitrated
1E (anion)	153	248	<0.6	297
1E'			15	311
2E (20:80)	134	245	0	n/a
3E (50:50)	131	239	<0.2	300
4E (cation)	0	n/a	0	n/a

Sample 1E corresponds to sample 3D above. A “grab” sample, designated 1E’, was taken just prior to the final 2-volume rinse with DI water. The substantially larger exothermicity for the unrinsed resin relative to the rinsed sample indicates that at least one rinse is necessary to complete the elution of the nitrate displaced by the last volume of salicylate. The composition of the unrinsed sample is comparable to sample 2D above. One surprising result of this experiment is that the exothermicities of all the fully nitrated samples (1E, 2E, and 3E) are so similar. Since the “nitrated” cation-exchange resin (4E) retained a negligible amount of nitrate, one may expect the exothermicities of mixed resin samples to correspond linearly with the percentage of anion-exchange resin. Note also that the onset temperatures decrease slightly as the percentage of cation-exchange resin increases. These data may indicate that cation-exchange resin is a better “feed stock” for the nitrate than anion-exchange resin and that mixed-resin stockpiles may be a slightly greater explosion/fire hazard. Fortunately, the salicylate exchange produces a final product with minimal exothermicity.

Resin Neutralization Step

Cation-exchange resins exist in the protonated state even after DI water rinse. Salicylic acid has only marginal solubility in water (0.016 M at room temperature), so solutions of sodium salicylate exposed to the acidic form of the cation exchange resins become protonated and precipitate out as salicylic acid on the resins. The sodium hydroxide rinse prevents precipitation of salicylic acid on the resin. The sodium hydroxide rinse is necessary only for the samples containing cation-exchange resins, but these also should be useful for neutralization of inadequately rinsed anion-exchange resins. It should also help “fix” the Pu as an oxide/hydroxide, and thus minimize the possibility of Pu elution along with the salicylate solutions.

Swollen-Bead-Size Determination

Experiment D was also used to determine the swollen volume for the Dowex 11 resins. A small ion-exchange column was calibrated with water (6 mm height = 1 mL volume). The average swollen-bead volume for fully nitrated Dowex 11 resin in DI water is 1.55(2) mL/g of resin (dry weight). This volume increases to 1.67(1) mL/g upon replacement of the nitrate with salicylate. This corresponds to an 8% increase in volume. Because the Dowex 11 resin used in these tests is highly cross-linked, it is expected that degraded Rocky Flats resins will exhibit a somewhat greater change in volume.

In Experiment E, mixtures of anion- and cation-exchange resins were found to undergo dramatic changes in volume (ca. 20%), going from DI water (large volume) to nitric acid (small volume) to the salicylated form (intermediate volume). Because the greatest change in volume is always exhibited with the first contact with sodium salicylate, it is recommended that the resins be slurried in a solution of sodium salicylate prior to loading into the ion-exchange columns, particularly if the sample is suspected of containing an appreciable fraction of cation-exchange resin.

Resin Capacity Determination

The solutions from Exp. D were assayed for salicylate. The amount of salicylate on the resins was calculated from the difference between the amount of salicylate added to the resins and the amount eluted. For the "fully salicylated" Dowex 11 sample, 3D (with lowest exothermicity), the calculated ion-exchange capacity is ca. 2.2 meq/g of resin. CHN analyses of the vacuum dried chloride and nitrate resin forms give an exchange capacity of 2.9 meq/g each.

"Hot" Column Experiments

Small-scale column experiments were run on the four anion- and cation-exchange resin combinations as in Exp. E above (100% anion, 20/80 cation/anion, 50/50 cation/anion and 100% cation). The columns (3/4" diameter polypropylene) were loaded in the "cold" labs and introduced into the glovebox line in the PF-4 Plutonium Facility. The full procedure for Pu-loading, elution, and resin denitration is given in Appendix 2. Briefly, the 5-g resin samples were each loaded with 5 mL of 16 mg/mL Pu(IV) in 7 M HNO₃. Excess Pu was eluted with 2 × 5 mL of 0.35 M HNO₃ followed by 2 × 5 mL of DI water. The effluents were collected for Pu analyses to determine the amount of Pu adsorbed to each sample (1I-4I). The resins were then eluted with 5 mL of 1.0 M NaOH, 5 mL of DI water, 3 × 5 mL of 2.0 M NaSal, and 2 × 5 mL of DI water. These effluents were collected for Pu analyses to determine the amount of Pu eluted in the denitration process (1F-4F) relative to the amount initially sorbed onto the resins. Samples of the resins before and after denitration were collected for DSC analyses.

The Pu assays for 1F-4F clearly show that the salicylate denitration process elutes only very small amounts of Pu. In fact, the Pu in the "final" samples was probably eluted just prior to the sodium hydroxide wash front. Results of the resin (Pu) loading, elution, and denitration are listed in Table 5.

Table 5. Anion- and Cation-Exchange Process Data

Sample ID	mg Pu eluted	mg Pu on resin	mg Pu/g of resin	% Pu eluted
1I - 100%anion	2.5	77.5	15.5	3.1
2I - 20%cation	10.1	69.9	14.0	12.5
3I - 50%cation	11.5	68.5	13.7	14.4
4I - 100%cation	12.6	67.4	13.5	15.7
1F - 100%anion	8.72E-02			0.11
2F - 20%cation	5.74E-02			0.08
3F - 50%cation	4.23E-01			0.62
4F - 100%cation	2.70E-01			0.40

All the resins were loaded to the 14-16 mg Pu/g resin levels, which are the maximum levels for Rocky Flats residues (approximately 1% of the ion-exchange capacity). As expected, the sodium hydroxide rinse helped "fix" the Pu onto the resin substrate, and the salicylate (which is a relatively poor complexing agent for Pu) appears to have a negligible effect upon Pu elution.

The DSC results for the “hot” samples are given in Table 6. The low exothermicity of the initial samples suggests that any extra nitrate bound with the Pu(IV) has minimal impact at these loading levels. In fact, the exothermicity of the fully nitrated resins is suppressed somewhat relative to their corresponding cold samples in Exp. E and they correlate qualitatively with the percent anion-exchange resin in the mixture. For three of the samples, the exothermicity of the final materials is too low to measure. The treated 100% cation-exchange resin (4F) exhibits a small, oddly-shaped exothermic peak at an unusually high temperature. It is possible that this peak is unrelated to the nitrate-resin interaction of interest.

Table 6. DSC Data - Exothermic Energy and Onset Temperatures

Sample ID	cal/g nitrated	onset temp °C nitrated	cal/g denitrated	onset temp °C denitrated
1I,F (100% anion)	135	250	0	n/a
2I,F (20% cation)	123	251	0	n/a
3I,F (50% cation)	102	249	0	n/a
4I,F (100% cation)	n/a	n/a	11	403

Large-scale Column Experiment

Nitration: One kilogram of 20/80 cation/anion resin mixture was prepared using Dowex 50Wx8 and Dowex 11 (chloride form). This resin was loaded into a 3" diameter ion-exchange column in 2 M HNO₃ to a height of 22". The resin was contacted with a total of 4 L of 2 M HNO₃ in order to nitrate the resin; it was then allowed to sit for three days. It was rinsed with 2 L of DI water and removed from the column into a 4 L polypropylene beaker. Samples of the resin were extracted from the top and bottom of the column for DSC analyses.

Denitration: In the interest of volume minimization, it was decided to combine the base neutralization step with the first sodium salicylate contact. The resin was slurried with 0.8 L of 2.0 M NaSal in 1.0 M NaOH. The pH was adjusted to basic (>9) by adding approximately 1 mL of 10 M NaOH, and the resin was transferred to the column with the remaining 200 mL of the 2.0 M NaSal in 1.0 M NaOH. The solution was eluted into a container at ca. 200 mL/min. This was followed by elution with 2 L of 2.0 M NaSal (pH~6) added to the resin via a peristaltic pump. The rate of addition/elution was slowed to 100 mL/min to minimize disturbance of the resin at the top of the column. The resin was then rinsed with ca. 1 L of DI water and allowed to drain. The final resin volume was about 6% greater than for the nitrated form. Resin samples for DSC analyses were collected from the top and bottom of the column.

Table 7 lists the results of the large-scale experiment. They correlate with those of the smaller-scale experiments. The high onset temperature for the final sample (top of the column) made it difficult to separate that small exothermic peak from the following endothermic peak (424°C), thus resulting in a range of integrated peak areas. The value of ~6 cal/g is a “best guess”.

Table 7. DSC Data - Exothermic Energy and Onset Temperatures

Sample	cal/g	onset temp °C
L-1 Nitrated – top of column	205	242
L-2 Nitrated – bottom of column	185	243
L-1 Denitrated – top of column	~6	351
L-2 Denitrated – bottom of column	0	n/a

Salicylate Recovery Procedure

The salicylate effluent from the large-scale experiment above was collected in two 4 L beakers each containing 2 L of ca. 2 M HNO₃/HCl (the waste acid from the resin nitration). The sudden exposure to acidic solutions precipitates the salicylic acid as a white, fluffy material that is easily filtered using a coarse- or medium-frit glass filter. Salicylate assay of the filtered solution (pH ~ 1) shows that the salicylate concentration is similar to that expected under equilibrium condition(Fig. 4).

Figure 4. Concentrations of HSal. and Sal. as a Function of pH.
Solubility data for salicylic acid is from the Merck Index, Ninth Edition.

The solid salicylic acid is recovered analytically pure, with any excess nitrate easily removed by rinsing with DI water. The table below outlines the components of the waste solution from the denitration of 1 Kg of 20/80 resin mixture.

Total volume of solution	4.5 L
pH of solution	0.9
Concentration of salicylate	0.009 <u>M</u>
Total salicylate in solution (moles)	0.0405
Total salicylate in solution (g)	5.6
Mass of recovered salicylic acid (g)	1450 g (wet)

The initial contact with 2 M NaSal in 1 M NaOH allows the resin to swell prior to loading into the column. The introduction of the salicylate recovery/recycle procedure depends heavily on the cost-effectiveness of the process. Sodium salicylate costs approximately \$20/kg. To process 280 kg of resin would require 270 kg of NaSal and generate 200 kg of “waste” salicylic acid. If the precipitated salicylic acid entrains eluted Pu, then disposal of large quantities of salicylic acid could be problematic. Therefore, recovery and recycle of excess salicylic acid is strongly recommended. The material is easily filtered and redissolved in NaOH. Small quantities of Pu or residual nitrate are unlikely to significantly decrease the effectiveness of the salicylate in the next denitration run.

Listed below are some recommendations for salicylate recycle.

- 1) Salicylic acid may be precipitated using more concentrated acid, but the solids:solution ratio must be kept low enough for good mixing.
- 2) Rinsing of the salicylic acid with DI water and vacuum filtration yields a cleaner product
- 3) Redissolve the salicylic acid in a minimum amount of 6 M NaOH then dilute to 2 M for the next use. This should minimize the amount of excess base used.

Potential Modifications of the Denitration Procedure

- 1) Going to batch processing rather than column processing decreases the overall effectiveness of the salicylate denitration procedure. However, if the higher exothermicity of the batch processed resin is still within acceptable guidelines, then the decrease in effectiveness is not a problem. Ease of operation and the allowable exothermicity of the final resin form will determine whether batch or column processing is preferred. Two or three contacts with 2 M NaSal, provide the bulk of the denitration; additional contacts do not appear to improve the final product.
- 2) The combination of the base neutralization step with the first salicylate contacts was aimed at waste volume minimization. Operators may find it more convenient to neutralize the resin with more concentrated NaOH then add the salicylate solution. Regardless, the resin must be slightly basic (pH>7) for the salicylate to be effective.

- 3) Other acids may be used to precipitate the salicylic acid. The large amount of excess nitrate from elution and using nitric acid (estimated 6.3 moles per kg of resin processed) produces a nitrate-rich aqueous waste that is well-above nitrate discard limits. Additionally, without large amounts of nitrate present, much of the remaining solubilized salicylic acid (ca. 0.01 M) may be removed from the aqueous waste stream using anion-exchange resins.

Based on the large-scale “cold” experiments and the small-scale “hot” experiments, we estimate the following for materials and waste stream composition:

	per kg resin	for 280 kg resin	assumptions
kg NaSalicylate needed	0.96	269	no recycling of salicylate
kg NaSalicylate needed	0.21	58	complete recycling of salicylate

Waste stream	per kg resin	for 280 kg resin	assumptions
g salicylate	6.2	1736	precipitation yields 0.01 M salicylate in discardable solution
g Pu	< 0.04	< 11.2	ave. of 2 e-4 g Pu eluted for the 5g samples is a “worst case” situation.
g nitrate	> 82 > 378	>22,960 > 105,840	1.3 moles nitrate per kg resin yields the smaller amount of displaced nitrate. Larger amounts assume nitric acid is used for salicylate precipitation.
volume of effluent (L)	4.5	1,260	may vary by as much as 20%
g Pu/ L	0.009	0.009	calculated from 0.04 g Pu/ 4.5 L effluent

Summary

Resin denitration via anion-exchange is an implementable process that can effectively mitigate the hazards associated with nitrated resins. Salicylate has been selected as the exchange anion of choice because of its superior selectivity for the Rocky Flats resins and its unique potential for comprehensive recovery and recycle. The final resin form should be amenable to cementation, incineration, pyrolysis, CWC0, or any other waste treatment.

APPENDIX 1

Ion-Exchange Equilibrium Calculations

The standard ion-exchange equilibrium reaction for similarly charged ions is given by:

$$K_{eq} = \frac{(n_B)[A]}{(n_A)[B]} \quad \begin{array}{l} n_A, B = \text{milliequivalents of anion on resin} \\ [X^-] = \text{solution conc. (Molar) of anion} \\ K_{eq} = K_B/K_A, \text{ where } K_B \text{ and } K_A \text{ are the selectivity coefficients on} \\ \text{Table 1} \end{array}$$

Conditions for each single contact of a resin loaded with anion A with a certain amount of anion B (determined by the volume, V_B , of a solution with molarity B) are outlined in the table below. The "initial conditions" are those upon adding the solution of B to the loaded resin. Note that the initial solution concentration of anion A is set to zero because excess solution is removed from the resin prior to each contact.

Initial Conditions

$$\begin{array}{l} n_A \\ n_B \\ [A] = 0 \\ [B] = B \end{array}$$

Equilibrium Conditions

$$\begin{array}{l} n_A = (n_A - x) \\ n_B = (n_B + x) \\ [A] = (x/V_B) \\ [B] = B - (x/V_B) \end{array}$$

The equilibrium conditions yield the following equation:

$$K_{eq} = \frac{[n_B + x][x/V_B]}{[n_A - x][B - (x/V_B)]}$$

Solving the quadratic equation for x provides two solutions, one of which is real.:

$$\begin{array}{ll} a = K_{eq} - 1 & x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ b = -n_B - (K_{eq}(n_A + BV_B)) & \\ c = (K_{eq})(n_A)(B)(V_B) & \end{array}$$

For example, the first contact of 1 g of the chloride form of Dowex II (exchange capacity of 1.1 meq/g) with 5 mL of 0.2 M HNO_3 ($K_{eq} = K_{\text{NO}_3}/K_{\text{Cl}} = 65/22 = 2.95$) sets the following conditions:

Initial Conditions

$$\begin{array}{l} n_{\text{Cl}} = 1.1 \text{ meq} \\ n_{\text{NO}_3} = 0 \text{ meq} \\ [\text{Cl}^-] = 0 \text{ M} \\ [\text{NO}_3^-] = 0.2 \text{ M} \end{array}$$

Final Conditions

$$\begin{array}{l} n_{\text{Cl}} = (1.1 - x) \text{ meq} \\ n_{\text{NO}_3} = x \text{ meq} \\ [\text{Cl}^-] = (x/5) \text{ M} \\ [\text{NO}_3^-] = 0.2 - (x/5) \text{ M} \end{array}$$

The “real” solution is $x = 0.66$, so the first contact displaces approximately 60% ($0.66/1.1$) of the chloride. The second contact has the following conditions:

Initial Conditions

$n_{\text{Cl}} = 0.44 \text{ meq}$
 $n_{\text{NO}_3} = 0.66 \text{ meq}$
 $[\text{Cl}^-] = 0 \text{ M}$
 $[\text{NO}_3^-] = 0.2 \text{ M}$

Final Conditions

$n_{\text{Cl}} = (0.44-x) \text{ meq}$
 $n_{\text{NO}_3} = (0.66+x) \text{ meq}$
 $[\text{Cl}^-] = (x/5) \text{ M}$
 $[\text{NO}_3^-] = 0.2 -(x/5) \text{ M}$

For the second contact, $x = 0.3$, so an additional 27% of the original 1.1 meq of chloride on the resin is displaced by nitrate. Such a decrease in displacement with subsequent contacts is an equilibrium phenomenon and is one reason why dynamic flow systems (such as columns) offer much greater displacement efficiencies.

Salicylate Assay Procedure

The following is a modification of the salicylate assay procedure included with the kits from Sigma Chemicals. Spectrophotometric assay is accurate for concentrations of salicylate ranging from 10 to 100 μM in the cell.

salicylate assay kit	Sigma Chemicals
salicylate standards	Sigma Chemicals
micropipettors	10 μL to 1 mL
volumetric flasks	five 10 mL

Calibration

- 1) Pipette 1 mL of the salicylate blank solution and 10 μL of colorimetric indicator into the volumetric flasks.
- 2) Pipette 0, 50, 100, 500 and 1000 μL of 100 mg/dL salicylate standard into each flask, respectively.
- 3) Dilute to the mark with DI water
- 4) Use the first flask as the blank. Measure the absorbance at 524 nm (or peak maxima) for remaining samples.
- 5) Plot absorbance vs. concentration and fit to a line to prepare the calibration curve.

Solution Assay

Run as above for the calibration. Dilute any samples that are too concentrated, but a 0.01 M solution of salicylate should give good results using a 200-500 μL sample aliquot.

APPENDIX 2

Procedure for Pu-loading, Elution, and Resin Denitration

Ion-exchange Column Set-up

- 1) Individual columns were prepacked in DI water prior to introduction into the glovebox.
Total resin = 5.0 g.
- 2) Columns were introduced into the glovebox line via an open-front hood.
- 3) Assembled columns use a ring stand for support.

Sample Loading/Elution Step

- 1) Pipetted 5 mL of 16 mg/mL Pu in 7 M nitric acid onto the wet resin. Elute as slowly as possible (>10 min/aliquot) into first vial. Let elute and sit while running other columns.
- 2) Eluted excess Pu solution using 2×5 mL of 0.35 M nitric acid.
- 3) Eluted column solution into the beaker using 2×5 mL of DI water.
- 4) Diluted solution (ca. 20 mL) in vial to the 50 mL mark. Capped and labeled as “#X init”.
- 5) Using a small spatula, transferred a small amount (ca. 200 mg) of the resin from the top of the column into a scintillation vials. Labeled as “#X init” and set aside for DSC analysis. Vials were left open to let dry.

Denitration Procedure

- 1) Pipetted 5 mL of 1.0 M NaOH onto resin. Eluted into second vial.
- 2) Rinsed with 5 mL of DI water.
- 3) Eluted with 3×5 mL of 2.0 M sodium salicylate solution at ca. 2 min/5 mL or less.
- 4) Rinsed resins using 2×5 mL of DI water. Eluted into beaker, letting column run dry.
- 5) Diluted solution (ca. 20 mL) in vial to the 50 mL mark. Capped and labeled as “#X final”.
- 6) Transferred resin from column to screw-top vials and mixed thoroughly. Using a small spatula, transferred a small amount (ca. 200 mg) of the resin into a scintillation vials. Label vials as “#X final”. Vials left open to dry for DSC analyses.
- 7) Discarded all excess solutions into 1-L waste container.

Equipment/Reagents:

- 1) 25 mL polypropylene disposable ion-exchange columns equipped with flow valves.
- 2) 50-100 mL of Pu(IV) in 7 M nitric acid at a level of ca. 16 mg/mL.
- 3) 50-100 mL of 0.35 M nitric acid for elution.
- 4) DI water for rinses and dilutions (500 mL in wash bottle).
- 5) 100 mL of 2.0 M sodium salicylate.
- 6) pH paper for monitoring pH of solutions.
- 7) Miscellaneous pipettes and vials for measuring and transferring volumes of solutions.
- 8) 100 mL beaker and 1 L polypropylene bottle for aqueous waste.
- 9) 60 mL polypropylene bottles w/ 50 mL calibration mark for standardization and storage of solutions for scintillation counting.
- 10) Ring stand with small clamp.
- 11) Test tube rack or large beaker for temporary column storage.
- 12) 5 mL pipet with tips.
- 13) Screw-top vials for resin storage.