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Removal of ^{137}Cs from Dissolved Hanford Tank Saltcake by Treatment with IONSIV® IE-911

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Abstract: This paper describes the removal of Cs from dissolved Hanford tank saltcake. A composite feed solution was prepared by dissolving archived saltcake samples from Hanford single shell tanks 241-S-101, 241-S-109, 241-S-110, 241-S-111, 241-U-106, and 241-U-109 and adjusting the solution to approximately 5 M Na^+. This composite feed solution was treated by ion exchange with IONSIV® IE-911, which effectively reduced the concentration of ^{137}Cs to a point of negligible contribution to the overall sample dose. The reduction in sample dose was sufficient for subsequent testing of waste immobilization technologies without significant radiological hazard. Among the major identified species was K^+, the principle cesium competitor in the ion exchange process, which was present at 0.01 M or about 550 times greater than cesium concentration. Ion exchange using IONSIV® IE-911 demonstrated high selectivity for cesium and quantitatively depleted ^{137}Cs from this feed, with an observed decontamination factor of greater than 30,000. The Cs-depleted saltcake solution also was characterized, and these results are compared to the initial characterization data when possible. As part of this characterization effort, the application of visible spectroscopy for quantifying major anionic components in tank waste was explored, and its potential as a means for directly measuring major bulk components in tank waste is discussed.

INTRODUCTION

Recently, the U.S. Department of Energy's Richland Operations Office (DOE-RL) prepared the Performance Management Plan for the Accelerated Cleanup

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of the Hanford Site (1). This plan proposes an accelerated cleanup for the Hanford Site, with one element of the plan being to complete the processing of the Hanford Site's high-level waste (HLW) by 2028. To meet this accelerated schedule, new technologies will need to be developed and implemented to supplement the capacity of the Waste Treatment Plant (WTP). Several technologies are being considered as alternative treatments of dissolved saltcake waste, and laboratory testing is required with actual dissolved saltcake from Hanford Site's single-shell tanks (SST) to assess these technologies.

Gasper et al. (2) identified 68 SSTs, each containing 50,000 gallons or more of saltcake, that are considered candidates for treatment by supplemental technologies. For laboratory testing, it is desirable to use a saltcake that is representative of the wastes contained within these 68 tanks. The saltcake sample described in this report was designed to meet this criterion for saltcake composition. This saltcake sample is a composite material, obtained by dissolving archived samples from Hanford SSTs 241-S-101, 241-S-109, 241-S-110, 241-S-111, 241-U-106, and 241-U-109 and adjusted to approximately 5 M Na (3). To reduce the radiation hazard during laboratory testing, the removal of ^{137}Cs (the primary source of penetrating radiation in these solutions) was desired. This paper describes the removal of ^{137}Cs from dissolved Hanford tank saltcake at Pacific Northwest National Laboratory by a column chromatography treatment using IONSIV® IE-911, an inorganic material based on a cesium-selective crystalline silicotitanate.

Some characterization of the initial feed solution and of the ^{137}Cs-depleted material is provided. During the characterization of the ^{137}Cs-depleted solution, we investigated UV-visible spectrophotometry as an alternative to ion-chromatography for the determination of chromate, nitrate, and nitrite concentrations in the depleted solution. An analysis of the oxidation-state speciation of chromium in the depleted sample by this technique also is reported.

EXPERIMENTAL SECTION

General

This section presents details concerning the operations for processing the dissolved saltcake. These operations include feed-solution collection, filtration and homogenization, IE-911 preparation for column use, a preliminary test of the IE-911 material's effectiveness at Cs removal, setup and shakedown testing of the IX column, and the actual processing of the filtered feed solution through the IE-911-containing column. Details are also provided concerning the measurement of the ^{137}Cs concentration in the column effluent while processing, and a description is provided of how ultraviolet-visible (UV-vis) spectroscopy was used to quantify selected anions in the combined column effluent.

All chemicals used were of reagent grade unless otherwise indicated. IONSIV® IE-911 (Lot # 8671-08), an engineered form containing a crystalline silicotitanate as the active Cs-binding material, was obtained from UOP (Des Plaines, IL). A gamma spectrometer with a liquid-nitrogen-cooled Ge detector was used to monitor ^{137}Cs activity by measuring the daughter ^{137m}Ba 662 keV emission after waiting for secular equilibrium to be re-established. Sodium hydroxide solutions were prepared by appropriate dilutions from a 50 wt % NaOH reagent solution in DI water using volumetric glassware. The targeted hydroxide concentrations were verified by titration with a standard HCl solution. All aqueous solutions were prepared using distilled water deionized to 18 MΩ cm with a Barnstead Nanopure water purification system.

The glass column (5 cm in diameter and 10 cm in height), the polyethylene tubing, and miscellaneous adapters used in the ion-exchange procedure were obtained from Spectrum Chromatography (Houston, TX). The variable-rate pump head (Part # Q1CKC), pump drive, and controller (Part # QVG50) used in the ion-exchange procedure were obtained from Fluid Metering, Inc. (Syosset, NY).

The UV-vis spectroscopic measurements were recorded on a 400 series charged-coupled device (CCD) array UV-vis spectrophotometer (Spectral Instruments Inc., Tucson, AZ). A PLASTIBRAND® cuvette with an extended optical transparency range from 220 to 900 nm was used for spectrophotometric measurements. The stock solutions of Na_2CrO_4, $NaNO_3$, and $NaNO_2$ needed for calibration experiments were prepared from reagent-grade chemicals dissolved in 0.1 M NaOH.

Analyses of solution metals concentrations were obtained by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Analyses of selected anions were accomplished by ion chromatography (IC). Total cesium concentration was determined by inductively coupled plasma-mass spectroscopy (ICP-MS). Selected radionuclides were measured: ^{241}Am, ^{152,154,155}Eu, ^{60}Co, and ^{137}Cs by gamma energy analysis (GEA) and ^{99}Tc by ICP-MS.

Preparation of the As-Received Feed Solution

The tested material is a composite of archived samples from Hanford SSTs 241-S-101, 241-S-109, 241-S-110, 241-S-111, 241-U-106, and 241-U-109. These archived samples were initially contacted with water; an aliquot was taken to determine the solution's sodium concentration; additional water was added to adjust the solution sodium concentration to its target of 5 M; and the adjusted solution was analyzed to verify the presence of a sodium concentration of approximately 5 M. The material was then allowed to settle for several days, and the supernatant was decanted, transferred into 24 250-mL glass jars for transport, and shipped to Pacific Northwest National Laboratory. Most of the bottles contained a clear liquid; however, 6 jars

contained perceptible amounts of gray solids. The contents of each jar were emptied into a 1 L filter device and vacuum filtered through a 0.2-micron polyethersulfone (PES) filter into a 1 L receiving flask. The filtered contents in the receiving flask were transferred into a tared, wide-mouth, 9 L, polyethylene bottle; and mass balance indicates that 6923 g of material were transferred.

After the filtered material was combined in the 9 L bottle, the solution was stirred mechanically for over 1 h. Two 20 mL aliquots of the homogenized liquid were then removed for selected analyses. Once filtered, no further precipitates were observed in the solution over a period of almost 4 months. The density of the homogenized, filtered-feed solution was measured as 1.253 ± 0.003 g/mL.

Conditioning and Characterization of IONSIV® IE-911

To determine the water content of the as-received resin, approximately 0.5 g of unconditioned IONSIV® IE-911 was placed in a 20 mL glass vial. The samples then were heated in an oven for 3 days at 105°C, allowed to cool, and reweighed. The F-factor, which is defined as the ratio of the dried solids weight to the initial solids weight, was calculated. Duplicate tests each gave an identical F-factor of 0.897.

To evaluate the performance of the IONSIV® IE-911 with the actual feed solution, the feed solution initially was sampled in duplicate to determine the initial ^{137}Cs activity. Batch contacts then were done, in duplicate, as follows. Approximately 0.25 g of IONSIV® IE-911 (IE-911) were placed in a tared, 20 mL glass vial and weighed. Then 10 mL of the filtered, combined, and homogenized feed solution were added, and the system was again weighed.

The vials containing the feed solution and IE-911 were placed in a rotary shaker and shaken at 150 rpm for 68.5 h at 25 ± 1°C. The shaking was stopped; the vials' contents were filtered through a 0.2 μm Nylon® syringe filter; and samples were removed to measure their ^{137}Cs activity. The batch-distribution coefficients (K_d) were then calculated according to the following formula (4):

$$K_d = \frac{(C_0 - C_i)}{C_i} * \frac{V}{(M * F)} \quad (1)$$

where

K_d = equilibrium batch-distribution coefficient (in mL solution/g dry solid),

C_0 = initial ^{137}Cs activity,

C_i = final ^{137}Cs activity,

M = mass of IE-911 (in grams) used in the batch-contact experiment,

V = volume of filtered feed solution (in mL) used in the batch-contact experiment,

F = F-factor for IE-911.

Column Testing

To acclimate the resin to the general conditions of the feed solution before testing, approximately 150 mL of IONSIV® IE-911 was suspended in 700 mL of 1 M NaOH in a 1 L bottle and agitated using a back-and-forth rocking motion for 2 h. The supernatant was decanted from the solids and discarded. Next, the solid was suspended in 700 mL of water and agitated as before for another 2 h, and the supernatant was again decanted off. This last step with water was repeated an additional five times to generate the conditioned material.

The ion exchange column system was assembled on a benchtop as illustrated in Fig. 1. 150 mL of the resin was loaded to the column. The dead volume in the assembly was determined to be 114 mL by measuring the time needed to fill the entire system with liquid at the fixed flow rate set by the calibrated flow-rate controller.

The performance of the system was examined periodically at different flow rates for several days after the dead-volume measurements but before use with the actual filtered feed solution. Two days after the dead-volume testing described above, a marked increase in the system's back pressure was observed, and a milky white stream exiting the column was noted. The system was disassembled, and the solids were sluiced repeatedly with DI water until the bulk of the readily suspended fine solids was

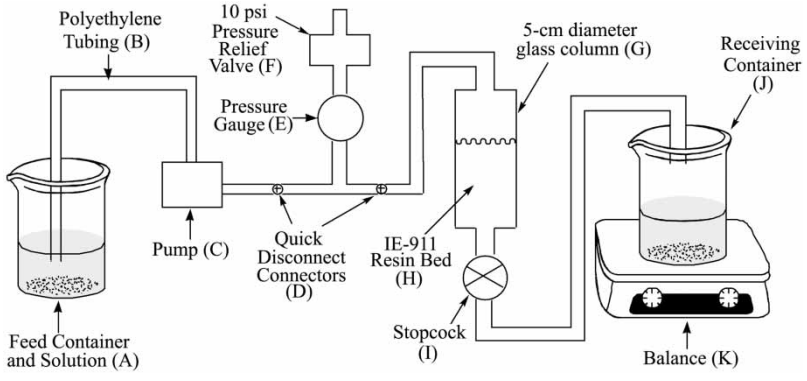

Figure 1. Schematic of hot cell IX system.

removed. No attempt was made to characterize either the fines or the milky solution. The system then was repacked and flushed extensively with DI water. Fines initially, but briefly, appeared in the column effluent, but these fine solids soon disappeared, and a clear liquid emerged. Repeated testing of the IX column apparatus was performed over the next several days. No further fines were observed, and no appreciable back pressure was observed with a flow rate up to 600 mL/h.

Immediately before testing with the feed solution, a 0.25 M NaOH solution was pumped through the system at 250 mL/h. The feed solution was introduced after a total of about 600 mL of 0.25 M NaOH was passed through the column. Upon introduction of the feed solution, the flow rate was reduced to about 200 mL/h and the feed-solution effluent collected in a tared receipt container. Periodically, the receipt container was weighed, and the effluent line was diverted to an empty glass sample vial to collect an approximately 3 mL aliquot for the Cs analysis. Monitoring the weight changes in the receipt container indicated that a steady flow of the effluent was occurring. Toward the end of the processing, with about 200 mL of material left in the feed-solution container, the feed tube shifted and moved out of the solution. Consequently, air was pumped into the system, and almost all the liquid remaining in the tubing and column passed into the effluent container and was replaced by air. The remaining 200 mL of feed solution was transferred to a small beaker, the feed tube was placed at the bottom of the beaker, and the remaining liquid was pumped through the system. Visual inspection of the system indicates that the column bed was not fully settled during contact with the feed solution for this final 200 mL; some air pockets were observed between the column surface and the column bed. No evidence of solids was observed in the column effluent.

After all of the effluent was collected into the receipt container, the effluent was homogenized by mechanical stirring overnight. The samples' ^{137}Cs activities from weighed aliquots of column effluent, as well as for a sample of the homogenized column effluent, were obtained. Duplicate 20 mL aliquots of the homogenized column effluent were withdrawn for chemical and radiochemical analyses.

RESULTS AND DISCUSSION

Generation and Analysis of the Feed Solution

The feed used in this study is a solution derived from a composite saltcake waste. The sodium concentration was adjusted to the targeted 5 M as shown by ICP-AES analysis of the feed solution (Table 1). This result agrees with an earlier, independently measured sodium concentration (3) of approximately 5 M. The measured density for the filtered feed solution of 1.253 g/mL also

Table 1. Analysis of major[a] bulk components in the feed and IE-911 processed solution

Analyte	Initial feed, Ave Conc., M	Processed solution, Ave Conc., M	% Agreement (final/initial)
Al	2.11E − 01	2.07E − 01	99
Ca	2.19E − 03	1.42E − 03	65
Cr	1.90E − 02	1.86E − 02	98
K	1.04E − 02	9.02E − 03	87
Na	5.14E + 00	5.10E + 00	99
P	5.80E − 02	5.32E − 02	92
Si	3.94E − 03	3.93E − 03	100
Cs	1.90E − 05	<9.77E − 08	<5.14E − 01
F^-	NP[b]	1.84E − 02	—
Cl^-	NP	4.15E − 02	—
NO_2^-	NP	4.13E − 01	—
Br^-	NP	1.63E − 03	—
NO_3^-	NP	2.44E + 00	—
PO_4^{3-}	NP	5.12E − 02	—
SO_4^{2-}	NP	9.32E − 02	—
Density (g/mL)	1.259	1.253	100
Free [OH^-], M	NP	0.51	—

[a]Defined here as being present in the initial feed at >50 μg/mL.
[b]NP = Measurement not performed.

agrees well with an earlier, independent, specific-gravity measurement (3) of 1.252 ± 0.002 g/mL. Prior to IE-911 treatment, the feed composition was analyzed for selected metals by ICP-AES, for total cesium concentration by ICP-MS, and for the radionuclides ^{241}Am, $^{152,154,155}Eu$, ^{60}Co, and ^{137}Cs by GEA and ^{99}Tc by ICP-MS. The results are summarized in Tables 1 and 2. Of particular interest is the concentration of potassium ion, which potentially could interfere with cesium for the active sites of IE-911 (9, 10), at 1.04E − 02 M, as compared to the measured concentration of total cesium at 1.9E − 05 M, for a K/Cs ratio of 550.

Batch Contacts with IONSIV® IE-911

IONSIV® IE-911 has been extensively investigated for the selective removal of cesium from DOE wastes, including column studies involving acidic tank wastes at the Idaho site (5), alkaline tank wastes at the Savannah River site (6), and alkaline tank wastes at the Oak Ridge site (7, 8). The results of performance testing with alkaline tank wastes have been recently summarized (9).

Table 2. Analysis of selected radionuclides in the feed and IE-911 processed solution

Analyte	Initial feed, Ave Conc., μCi/mL	Processed solution, Ave Conc., μCi/mL	% Agreement (final/initial)
^{99}Tc	3.99E − 02[a]	5.42E − 02	136
$^{99}TcO_4^-$	NP[b]	4.22E − 02	—
^{60}Co	5.62E − 03	6.81E − 03	121
^{137}Cs	4.66E + 01	1.21E − 03	2.6E − 03
^{152}Eu	NP	1.71E − 04	—
^{154}Eu	NP	8.89E − 03	—
^{155}Eu	NP	4.66E − 03	—
Total α	NP	7.15E − 03	—

[a]Due to a quality control failure, it is likely that this value is about 25% low.
[b]NP = Measurement not performed.

The IE-911 batch used, Lot # 8671-08, was an early formulation used in a prior test with supernatant from Tank 241-AW-101 (4). To verify that acceptable decontamination factors could be obtained with this material batch upon contact with this feed solution, batch contacts were performed using the actual filtered feed solution.

The measured Cs K_d (1170 mL/g) is 165% higher than the batch-contact Cs K_d reported in Brown et al. (4), where a value of 710 mL/g was reported but between two to three times lower than the K_d values of 2500–3000 mL/g observed in a test with Savannah River site tank 44F waste diluted to 5.4 M (6). Since the cesium distribution depends not only on the equilibrium Cs concentration but also on the concentrations of competing ions such as potassium (9, 10), one-to-one comparisons to these previous studies are of limited use. The important result of these batch K_d measurements is that the observed K_d indicates that this material, despite several years of storage, should still be able to effectively remove cesium from the filtered feed solution. The measured K_d value can be used to predict the IONSIV® IE-911 column performance.

IONSIV® IE-911 Column Behavior with the Feed Solution

The relatively wide, 5-cm-diameter column used in this work was chosen so that a low superficial velocity (the distance the surface moves during a given period of time) can be used to process the solution and still complete the processing in a timely manner. Lower superficial velocities also generally translate into more effective component removal. The superficial velocity used in the processing of this solution is low compared to previous studies; the 200 mL/h flow rate translates into a superficial velocity of

only 0.17 cm/min. During previous studies with superficial velocities of 0.27–1.06 cm/min, 100 to more than 500 column volumes of solution were processed before any increase in effluent cesium concentration was observed (9). Such comparisons are inexact because of differing component concentrations and formulations of IE-911 tested. Still, by limiting the number of bed volumes needed to process this solution, as well as by using a low superficial velocity, the system was designed intentionally to maximize cesium removal and was not designed to establish a breakthrough elution curve for comparison to other studies.

The processing was qualitatively monitored periodically by examining aliquots of column effluent for ^{137}Cs activity, and the results were generally as expected, with high ^{137}Cs depletion from the feed solution being observed. Table 3 summarizes the observed C/C_0 factors.

In several instances, no visual signal at 662 keV could be observed even after counting for 100 min; for these measurements, no ratios of the measured ^{137}Cs concentration divided by the initial ^{137}Cs concentration (C/C_0) can be reported. In essence then, except for the initial and final processing samples, no detectable ^{137}Cs appeared in the column effluent. The reasons for the presence of cesium in the initial and final processing samples may be similar. Initially, despite the several bed volumes of alkaline solution passed through the column before the feed solution was introduced, the

Table 3. Summary of measured ^{137}Cs activity in column effluent during processing

mL Feed solution processed	Est. Cumulative bed volumes Processed[a]	Estimated superficial velocity (cm/min)	Measured ^{137}Cs activity (cpm/g eluate)	C/C_0
0	0	NA	70,162	1.00E + 00
90	0.6	1.53E − 01	3	4.25E − 05
338	2.3	1.80E − 01	2	2.72E − 05
896	6.0	1.58E − 01	1	7.65E − 06
1,499	10.0	1.70E − 01	ND	—
2,113	14.1	1.74E − 01	ND	—
2,715	18.1	1.70E − 01	ND	—
3,316	22.1	1.70E − 01	ND	—
3,898	26.0	1.64E − 01	ND	—
4,527	30.2	1.78E − 01	1	1.06E − 05
5,272	35.1	1.46E − 01	6	8.90E − 05
Final composite	NA	NA	2	3.15E − 05

NA = Not applicable.
ND = No signal detected.
[a]neglects prior analytical samples taken.

column bed might not have been fully settled, and some channeling of the feed solution through the column may have occurred. Between the 4.5 and 5.3 L sampling events, the feed tube was displaced from the solution, and air was passed through the system. Consistent with visual observation, the bed might not have been fully settled when the final amounts of feed solution again were passed through the system, resulting again in a small amount of channeling. However, despite any cesium-removal inefficiencies associated with this possible channeling, the processing of the filtered feed solution through the IE-911 column resulted in a composite with good ^{137}Cs decontamination, with an overall C/C_0 of 3.15E − 05 corresponding to an overall decontamination factor of greater than 30,000.

Major Bulk Component Concentrations Before and After Treatment with IE-911

The results of the IC and ICP-AES measurements for the major bulk components are reported in Table 1. The average component value in the effluent, the molarity of the same component in the initial solution, if measured, and the percent of the component remaining in the solution following processing for Cs removal are provided.

The results outlined in Table 1 indicate that the bulk solution composition, with the exception of Cs removal, was little altered by contact with IONSIV® IE-911. Only significant depletion in the concentration of Ca was observed. Some removal of Ca by IE-911 from Hanford Site tank supernatants has been reported previously (4, 9). The relatively poor removal of potassium is surprising; potassium has been reported to possess some affinity for IE-911 (9, 10). The results in Table 1 provide information typically not reported in other studies of IE-911 column studies; in previous studies, attention has been focused on Cs and other radionuclide removal rather than an examination of other components.

The results of measurements for selected radionuclides are reported in Table 2. The average solution activity in a component, the activity of the initial solution in the same component, if measured, and the percent of the component remaining in the solution following processing for Cs removal are provided.

The specifically identified radioisotopes are those commonly associated with tank supernatants, ^{60}Co, ^{152,154,155}Eu, ^{241}Am, and, of course, ^{137}Cs. In general, most of the gamma activity in tank supernatants comes from ^{137}Cs. Processing of the feed solution through an IE-911 column has markedly reduced the ^{137}Cs activity in the processed solution. Indeed, it is no longer even the major source of activity in solution, with more (based on activity) ^{154,155}Eu, ^{241}Am, and ^{60}Co now present in the processed solution.

Spectrophotometric Analysis of the Final, Cs-Depleted, Feed Solution—Determination of Chromate, Nitrate, and Nitrite

We took the opportunity provided by the analysis of the Cs-depleted feed solution to investigate UV-vis spectroscopy as an alternative method to simultaneously determine concentrations of the major bulk tank waste components nitrate, nitrite, and chromate in this complex matrix. The analysis of a mixture of components is a common analytical problem in spectrophotometry. If the spectra of pure components are available, the spectrum of a mixture can be analyzed to determine the concentrations of the individual components. If the mixture contains N components, then absorbance measurements at N suitable wavelengths are necessary to solve the set of N linear equations in N unknowns. The application of this approach to the Cs-depleted feed solution is given below.

To analyze a mixture of chromate, nitrate, and nitrite, it is sufficient to measure the optical density of the composite at three different wavelengths. The spectra of the individual ions and of a Cs-depleted feed solution are shown in Figs. 2 and 3, respectively.

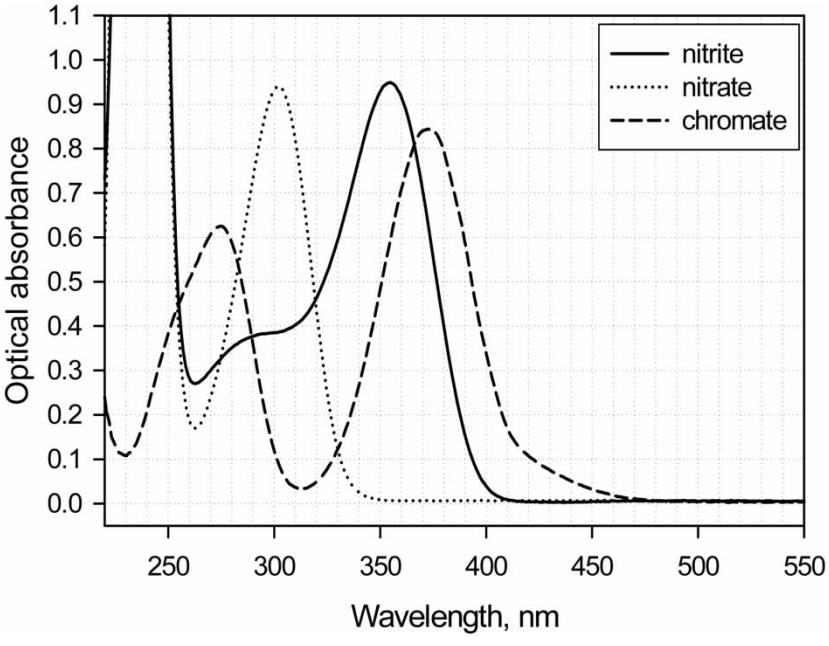

Figure 2. Spectra of nitrate, nitrite, and chromate at 122.8 mM, 38.46 mM, and 0.164 mM concentrations, respectively, in 0.1 M NaOH solution (optical path length is 1.055 cm).

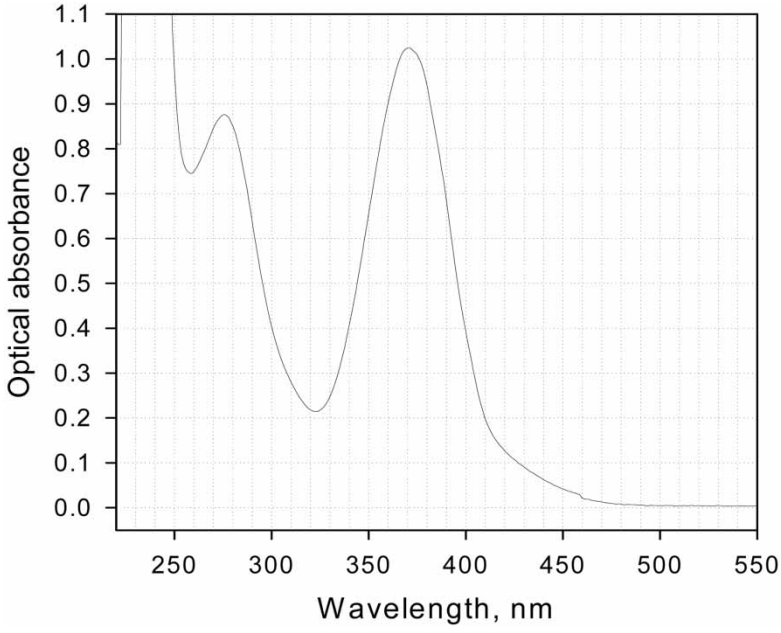

Figure 3. Spectrum of the final composite solution after a 101-fold dilution in 0.1 M NaOH.

The most suitable wavelengths for analysis are 302, 354, and 372 nm as determined from an examination of the most intense peaks' maxima positions.

The Beer's law for this three-component mixture can be written as shown below:

$$\varepsilon_{302}^{chromate} \times [chromate] + \varepsilon_{302}^{nitrate} \times [nitrate] + \varepsilon_{302}^{nitrite} \times [nitrite] = A_{302}/l$$
$$\varepsilon_{354}^{chromate} \times [chromate] + \varepsilon_{354}^{nitrate} \times [nitrate] + \varepsilon_{354}^{nitrite} \times [nitrite] = A_{354}/l$$
$$\varepsilon_{372}^{chromate} \times [chromate] + \varepsilon_{372}^{nitrate} \times [nitrate] + \varepsilon_{372}^{nitrite} \times [nitrite] = A_{372}/l$$

where ε and A are molar absorptivity and optical absorbance of the solution at the selected wavelength, values in square brackets refer to the species molar concentration in the solution, and l is the optical path length of a spectrophotometric cell (a plastic cell with $l = 1.055$ cm was used in spectral measurements described in this section).

The molar absorptivities of the three species at the specified wavelengths are given in Table 4.

A graphical deconvolution of the spectra is summarized in Fig. 4. From this analysis, the chromate concentration in a diluted sample solution was determined to be 0.184 ± 0.006 mM. Without taking into account the

Table 4. UV-vis data

	Molar absorptivity × l, M^{-1} (l = 1.055 cm)			
λ(nm)	CrO_4^{2-}	NO_3^-	NO_2^-	A, Cs-depleted feed solution
302.49	583	7.7	10.06	0.3642
353.75	3,465	0.01	24.5	0.7542
372.38	5,116	0.001	16.55	1.0204

interfering absorbances from nitrate and nitrite, the concentration of chromate calculated from its absorbance peak intensity at 372 nm in Fig. 3 (A = 1.02) would be overestimated by 8.5%. Similarly, the concentrations of nitrate and nitrite are found to be 27.2 ± 0.2 mM and 4.73 ± 0.13 mM, respectively. After correcting for sample dilution, the chromate concentration in the Cs-depleted feed solution is measured as 0.0186 ± 0.0006 M, the nitrate concentration as 2.74 ± 0.02 M, and the nitrite concentration as 0.48 ± 0.01 M. The latter two concentrations are in reasonable agreement with the IC results, which report a nitrate concentration of 2.44 ± 0.37 M and a nitrite concentration of 0.413 ± 0.06 M.

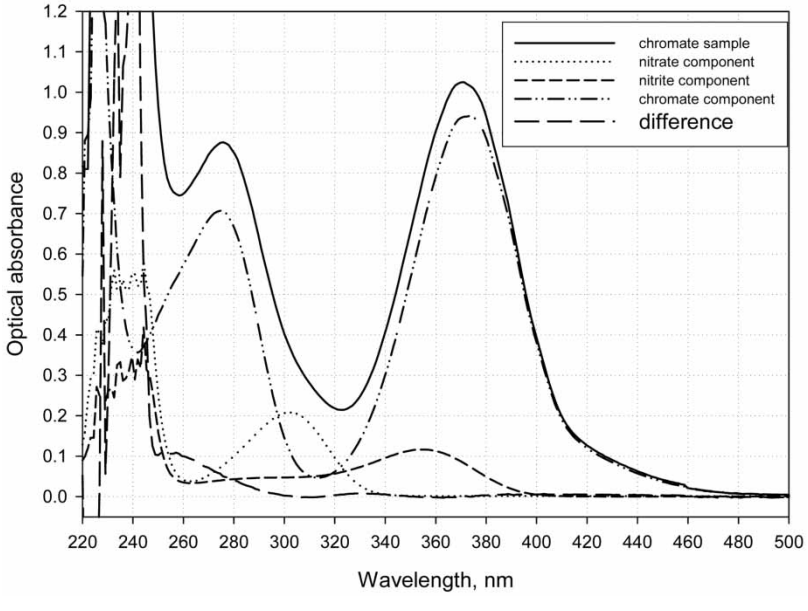

Figure 4. Deconvolution of the Cs-depleted feed solution spectrum into its separate components.

Comparison of the measured chromate concentration with the value of the total chromium concentration determined by ICP-AES (0.0186 ± 0.0028 M) indicates that there is no statistically significant concentration difference between the two values. However, additional analysis of the visible spectrum can directly address the relative oxidation states of chromium in the solution by analyzing the 372 nm region of the diluted feed solution, where the absorbance for chromate is at a maximum and 590 nm, where a major absorbance for $Cr(OH)_4^-$ is centered. The molar absorptivity of the latter species is much weaker than that of chromate and required spectral analysis of an undiluted solution to reveal its possible presence.

Figure 5 provides the visible spectrum for the undiluted Cs-depleted feed solution in the region from approximately 425 nm to 950 nm. An expanded scale is shown as an insert. A weak, but distinct spectral feature, is evident with an observed maximum at 570 nm. This wavelength position is 20 nm off compared with the 590 nm of $Cr(OH)_4^-$ species, but this difference might be attributable to the superposition of the tail from the main peak of chromate centered at 372 nm. The absorbance from the latter is so intense with a chromate concentration of 0.0186 M that its presence can be seen even some 200 nm away from the maximum. Qualitatively, superposition of the weak and broad 590 nm peak onto a steep tail from the 372 nm peak would be expected to affect the spectral shape of the former by shifting the apparent maximum to a shorter wavelength.

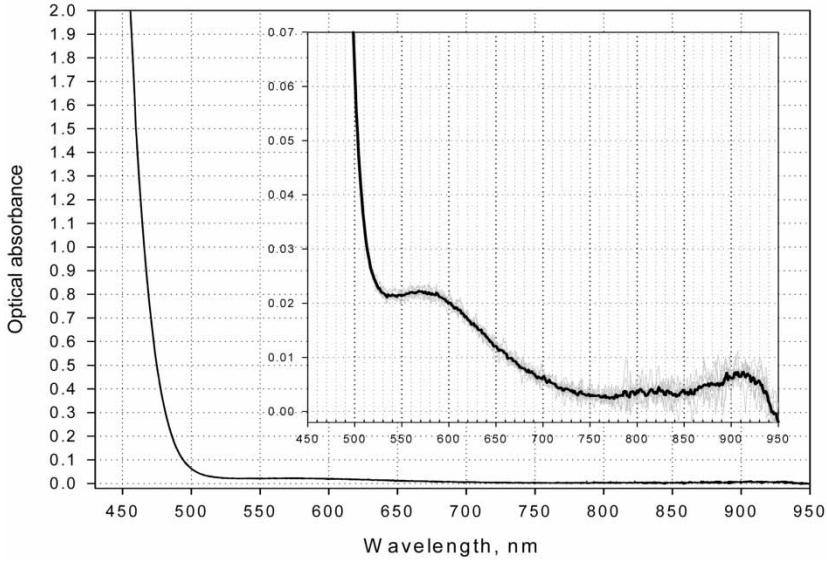

Figure 5. Optical absorbance spectrum of undiluted Cs-depleted feed solution. Gray traces represent nine single scans. The bold line is the averaged spectrum.

To see whether this assumption may explain the observed 20 nm difference in the spectrum of the proposed contribution from tetrahydroxychromate, a 0.0186 M solution of chromate in 0.1 M NaOH was prepared; its spectrum is shown in Fig. 6. It is apparent that the chromate absorbance levels off to the horizontal baseline at zero absorbance starting from 540 nm. It further indicates that all residual absorbance at 570 nm (A = 0.022) should come from the suspected anionic $[Cr(OH)_4]^-$. Such a level of optical absorbance would formally correspond to a $0.022/25.4 = 8.66\ 10^{-4}$ M concentration of Cr(III), which would indicate that as much as 4.5% of the total chromium concentration is present as the Cr(III) species. However, an attempt to recreate the experimentally observed spectrum at these concentrations of Cr(VI) and Cr(III) does not give an adequate correspondence between the real and the "synthetic" spectrum. If Cr(III) were the only species contributing to the overall absorbance in the 540–700 nm range and if its concentration were of $8.66\ 10^{-4}$ M, then the valley at 530 nm should be seen much more clearly (red trace in Fig. 6) vs. the local maximum at 585 to 590 nm. To put it in a more quantitative language, A_{530} should be not higher that 0.012, as opposed to actual observation of $A_{530} = 0.022$.

Two assumptions available to explain this discrepancy are (1) the chromate spectra in pure 0.1 M NaOH solution and in the complex mixture of 2.7 M of nitrate, 0.48 M of nitrite, and a number of other inorganic and organic constituents are not identical, and they exhibit a more pronounced

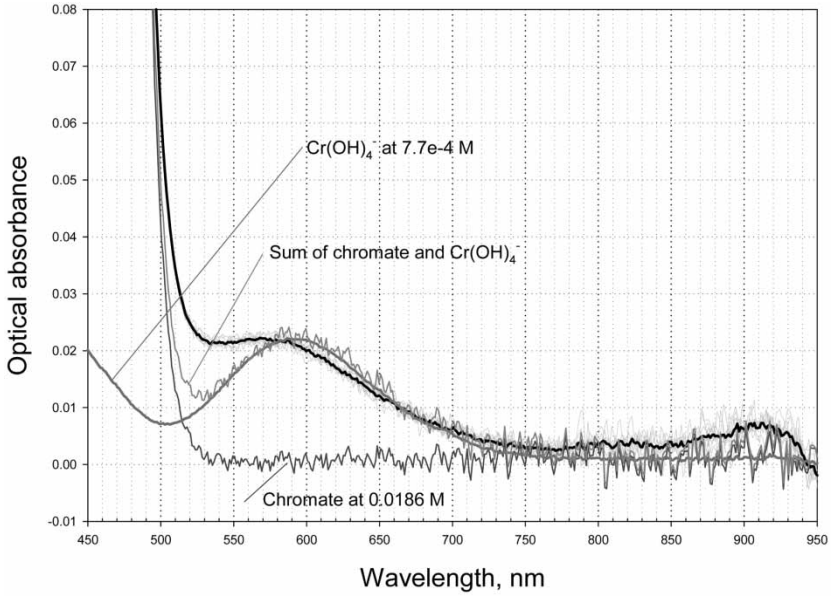

Figure 6. Spectral feature analysis with the assumption that chromate and tetrahydroxochromium(III) only contribute to the observed spectrum.

longer wavelength tailing effect in the latter case and (2) there is one more light-absorbing species, not associated with chromium, that manifests itself in the 540–700 nm range. Further experiments are required to prove these assumptions. What is more important for a more realistic estimation of the Cr(III) concentration is that both assumptions imply that the optical absorbance at 570 nm is only partly associated with Cr(III); and, thus, its contribution to the total chromium concentration in the analyzed solution is significantly less than the upper limit of 4.5% obtained from the two-component analysis.

CONCLUSION

The treatment of a composite feed solution, derived from dissolved actual Hanford Tank saltcake, with IONSIV® IE-911 effectively reduced the ^{137}Cs concentration. This reduction in the cesium concentration allowed for subsequent testing of waste immobilization without significant radiological hazard. Little perturbation of any other major constituents was observed.

Some methods-development work was also performed to explore the possibility of using UV-visible spectroscopy to determine the concentrations of nitrate, nitrite, and the speciation of chromium between its +3 and +6 oxidation states. The results obtained by UV-vis spectroscopy for nitrate and nitrite compare well (about a 10% discrepancy) with the concentrations determined by ion chromatography. Agreement with the total concentration of chromium as determined by ICP-AES is excellent, with almost identical concentrations measured for both total chromium and chromate. This spectrophotometric method shows potential for further use in analysis of tank supernatants, perhaps as an online monitor in the field to determine the behavior of nitrate, nitrite, and chromate during retrieval in real time. Finally, analysis of +3 vs. +6 speciation of chromium in this alkaline tank waste solution indicates that >95% of the chromium in this tank waste is present as chromate, a result consistent (but at a higher precision) with other studies on Hanford Site tank supernatants and leachate solutions, which were based previously on comparisons of the chromate to total chromium concentrations (11).

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