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Final Report: Recovery of Silver from CEPOD Anolyte Solutions

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Summary

The process known as Catalyzed Electrochemical Plutonium Oxide Dissolution (CEPOD) has been shown effective for removing plutonium from a variety of residues and solids (Bray and Ryan 1982; Wheelwright et al. 1991). This process involves the electrochemical oxidation of PuO_2 (and other Pu species) to $(PuO_2)^{2+}$, and dissolution of the latter species in the anode solution (anolyte). Silver ion is used to transfer charge from the electrodes to the solid Pu oxide. The same process may be used to destroy various organic materials.

Because silver is a Resource Conservation and Recovery Act (RCRA) land ban chemical, its removal from waste streams is highly desirable. Recovery and reuse of silver from solutions and waste streams is also of economic interest. Experiments were undertaken at the Pacific Northwest Laboratory for the U.S. Department of Energy to determine the feasibility of silver removal and recovery. Initial bench-scale studies using simulated CEPOD anolyte demonstrated the simple and effective removal of silver from CEPOD solutions to levels below the RCRA mandated limit of 5 parts per million (ppm). Ascorbic acid ($C_6H_8O_6$) was used to reduce silver ion to metallic silver, which precipitates from solution. Hydrazine, hydroxylamine, urea and sulfamic acid were tested for their ability to suppress nitrite, which depletes the reducing agent. Only trace (parts per billion) quantities of contaminant metals were found in the recovered silver metal.

Recent experiments confirmed the practicality of the process on a larger scale. Hydrazine (NH_2NH_2) and hydroxylamine (NH_2OH) were used to suppress nitrite in the initial experiments. The silver ion in 6 L of CEPOD anolyte (used previously for oil and paper destruction) was removed to less than 1 ppm. The silver ion was also removed from a total of 7.5 L of CEPOD anolyte that contained plutonium and other radioactive species. The process is believed to require less than 45 min. These experiments demonstrated the feasibility of silver ion removal on a process scale for both radioactive and nonradioactive solutions and provided the starting parameters for scale-up. The removal of silver from CEPOD solutions was easily and effectively accomplished. Thus, the presence of silver in the CEPOD process does not impair its utility as a waste treatment alternative.

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1.0 Introduction

The process known as Catalyzed Electrochemical Plutonium Oxide Dissolution (CEPOD) has been shown effective for removing plutonium from a variety of residues and solids (Bray and Ryan 1982; Wheelwright et al. 1991; Ryan et al. 1992).[(a)] This process involves the electrochemical oxidation of PuO_2 (and other Pu species) to $(PuO_2)^{2+}$, and dissolution of the latter species in the anode solution (anolyte). Silver is used to transfer charge from the electrodes to the solid Pu oxide. Ag (I) is oxidized at the anode to Ag(II) and carried by the solution to the plutonium oxide solids, where the silver and oxide undergo a redox reaction that converts Pu(IV) to Pu(VI), and Ag(II) to Ag(I). Other metal ions [such as Ce(IV) and Co(III)] may also be used for this charge transfer, but have been found to be less effective than silver. The same process may be used to destroy various organic materials (such as paper and wood, oil and fuels, and synthetic polymer materials) by complete oxidation to CO_2 or H_2O, for example (Wheelwright et al. 1991).

Upon completion of a CEPOD dissolver run, the anolyte may be processed to remove solution species of interest (i.e., Pu), or the anolyte may be recycled, or disposed. Because silver is a Resource Conservation and Recovery Act (RCRA) land ban material, it must be removed from waste streams. Recovery and reuse of the silver is also of economic interest. For these reasons, experiments were undertaken by Pacific Northwest Laboratory (PNL)[(b)] to determine the feasibility of silver removal and recovery. Preliminary experiments, completed in FY 1991, demonstrated a simple, effective technique for silver removal from solutions. Ascorbic acid ($C_6H_8O_6$) was used to reduce silver ion to metallic silver, which precipitates from solution. The influences of nitric and nitrous acid concentrations, which inhibit the reaction, were also noted. The process was demonstrated effective on a bench scale using samples of actual CEPOD anolyte. Further experiments, in FY 1993, optimized these parameters and demonstrated the effectiveness of the technique on CEPOD anolyte on a larger, process scale (liters of solution). This report describes both the preliminary bench-scale experiments and the more recent process-scale experiments. The results are also compared to electro-deposition, another method of silver ion removal.

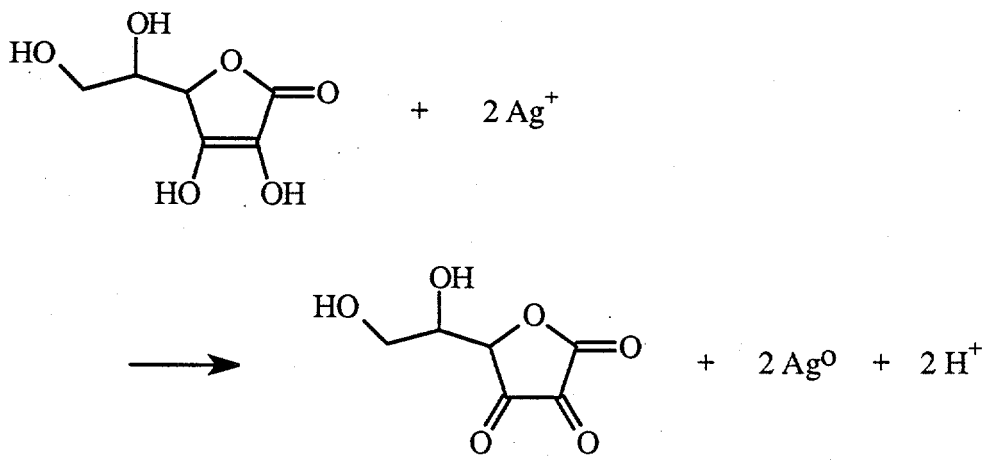
(a) Surma et al., 1993.

(b) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

2.0 Preliminary Experiments

2.1 Background

Preliminary experiments at PNL have shown that ascorbic acid ($C_6H_8O_6$) is a rapid and effective reducing agent for silver ion. The reaction is initiated immediately upon ascorbic acid addition, with the bulk of the silver in solution precipitating as the metal within minutes:



Further, silver ion is successfully removed from waste stream effluents to well below the regulatory limit of 5 ppm. However, the success of silver reduction in a nitric acid medium depends on control of the autocatalytic nitrite (nitrous acid, HNO_2) reaction. Nitrite in solution oxidizes ascorbic acid, rendering the reducing agent ineffective. Control is achieved by adding a nitrite suppressor reagent.

In preliminary experiments, four nitrite suppressor reagents were tested for their ability to control nitrite generation in nitric acid solutions of varying acidity: hydrazine, hydroxylamine, urea, and sulfamic acid. Based on their respective molecular structures and free energies of reaction, reactivity of the various nitrite suppressors toward nitrous acid was expected to proceed in the following order:

Hydrazine	>	Hydroxylamine	>	Urea	>	Sulfamic Acid
N_2H_4		$H_2N\text{-}OH$		$(NH_2)_2C = O$		$H_2N\text{-}SO_3H$

Qualitative observations in the preliminary experiments suggest that the above reactivity series is correct relative to nitrous acid.

2.2 Test Solution Experiments

A preliminary silver recovery experiment (using ascorbic acid as a reducing agent) performed by GH Bryan and JL Ryan at PNL (FY 1990) showed that less silver was recovered from nitric acid test solutions as the acidity was increased. Data obtained in this experiment are presented in Table 2.1.

Neither the time nor reagent concentrations (ascorbic acid and urea nitrite suppressor) for these experiments were precisely controlled, given the simple objective to show silver reduction (e.g., Ag^+ to Ag) was possible in a nitric acid medium. Approximately 24 h was required for significant silver recovery in these experiments. This lengthy reaction time was viewed as a major drawback to a process-scale silver recovery scheme. Subsequent experiments indicated that the kinetics of silver reduction are rapid (minutes) in acid solutions below 2 mol/L; silver reduction (and recovery) is slow (hours) only at HNO_3 concentrations above 5 mol/L, in agreement with previous runs. Given the slow reduction of silver ion to base metal in acid solutions above 5 mol/L, all subsequent experiments focused only on solutions containing from 1 to 4 M nitric acid.

Silver recovery is very dependent on the concentration of the reducing agent (ascorbic acid) and the solution acidity (nitric acid content). Figures 2.1 and 2.2 present the results of a second round of experiments that demonstrate this dependency. Unrecovered silver as a function of nitric acid concentration is shown for the various nitrite suppressors in Figure 2.1. For these runs, the concentration of the reducing agent (ascorbic acid) was initially 0.12 M. Figure 2.2 gives the results of a similar experiment in which the initial ascorbic acid concentration was 0.20 M. [Silver and nitrite suppressor reagent concentrations were each 0.10 M in the initial solution. Six hours reducing time was allowed between ascorbic acid addition and supernate filtration. The inductively coupled plasma-atomic absorption (ICP-AA) detection limit for silver is ± 50 ppb, and the 5 ppm concentration limit is indicated with a dashed line.]

It is immediately clear in both figures that more silver was left unrecovered in solution as the nitric acid concentration increased. Satisfactory recovery was observed for all nitrite suppressors for the 1 M nitric acid concentrations. In contrast, none of the tests exhibited successful silver recovery at 4 M nitric acid concentration, and results were mixed for the intermediate concentrations. Hydroxylamine and sulfamic acid were the most effective over the full range of conditions.

Table 2.1. Effect of Nitric Acid Concentration on Silver Removal

Nitric Acid Concentration(Mol/L)	Supernate Silver Concentration (ppm)
1	3
5	5
8	10

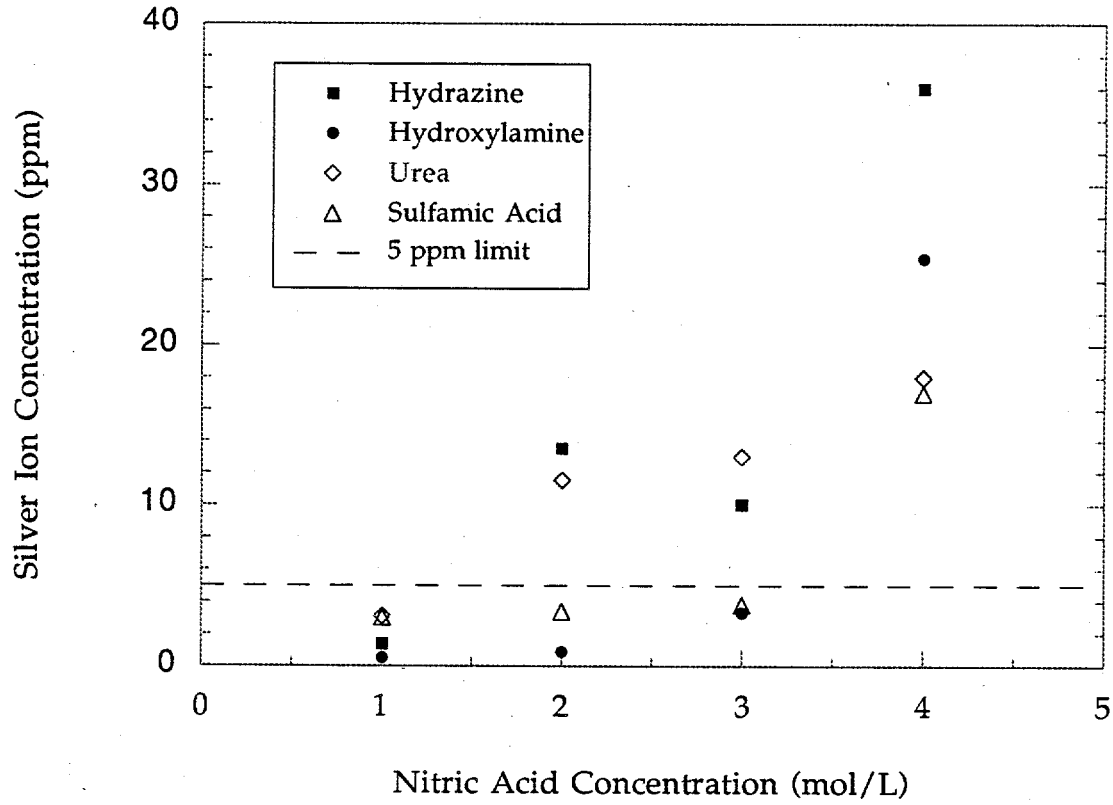


Figure 2.1. Effect of Nitric Acid Concentration on Silver Removal, 0.12 M Ascorbic Acid. Initial silver and nitrite suppressor concentrations were both 0.10 M. Initial ascorbic acid concentration was 0.12 M. Results for various nitrite suppressors (indicated in the figure) are shown.

A decreasing silver reduction rate with increasing acidity was also noted (qualitatively by the rate of precipitation of silver metal) in these same experiments. This latter observation is believed to be evidence of a hydrogen ion dependence on reduction rate.

The theoretical reducing capacity of ascorbic acid to silver is 2 equivalents/mole of reagent (two reducing sites per molecule). However, a comparison of the concentration of unrecovered silver for a given acid concentration and nitrite suppressor shows that the amount of silver left unreduced depends on the reducing agent concentration *in excess of the stoichiometric concentration*. A two-fold molar excess (four-fold reducing capacity excess) of reducing agent (0.20 M) to silver increased recovery results (relative to the equimolar case) anywhere from 30 to 3,000%. The apparent decrease in ascorbic acid reducing capacity in nitric acid is attributed to partial decomposition of the reagent; nitrous acid has been shown to accelerate this decomposition. Continued reagent oxidation by nitric acid is noted by the progression in residue formation in the supernate; no changes in supernate disposition occur in the absence of reducing agent.

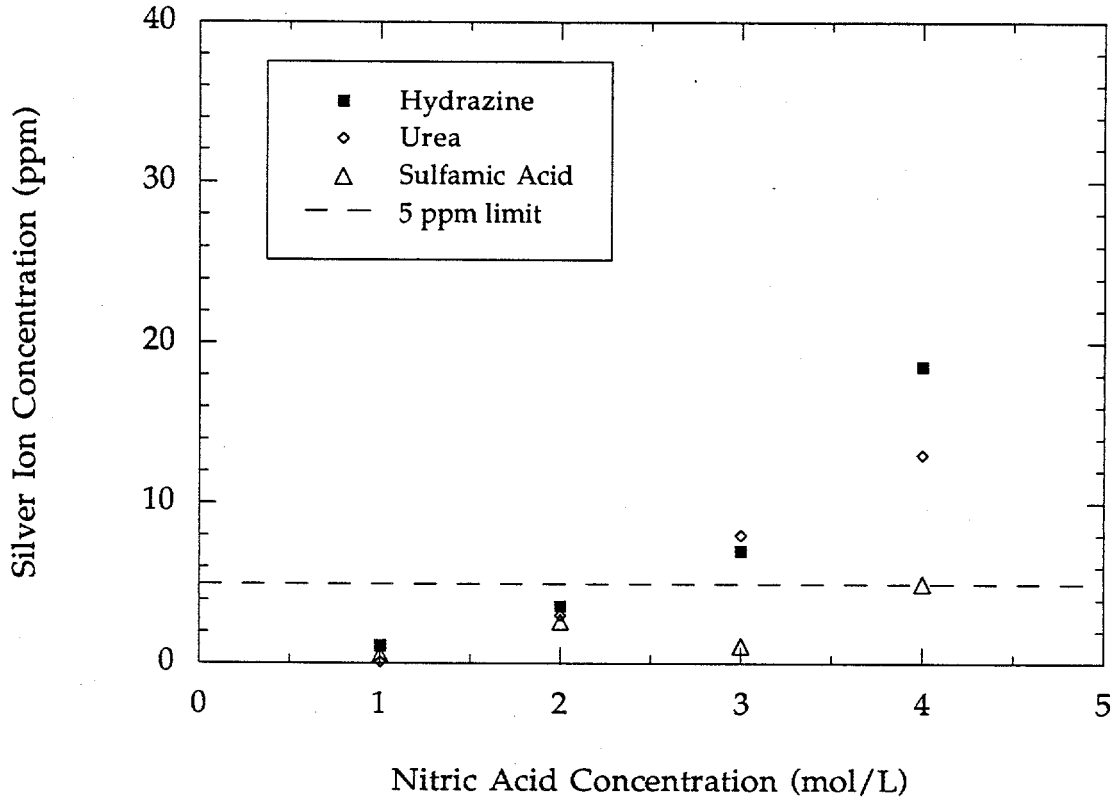


Figure 2.2. Effect of Nitric Acid Concentration on Silver Removal, 0.20 M Ascorbic Acid. Initial silver and nitrite suppressor concentrations were both 0.10 M. Initial ascorbic acid concentration was 0.20 M. Results for various nitrite suppressors (indicated in the figure) are shown.

Qualitative differences in relative reactivity rates toward nitrous acid were noted for the suppressor reagents investigated in this study. Both hydrazine and hydroxylamine, for example, reacted immediately with nitrous acid, as evidenced by vigorous effervescence, disappearance of typical nitrous acid color (yellow), or gas generation following reagent mixing. Urea, conversely, required from 30 to 60 min from time of dissolution to ascorbic acid addition to prevent reducing agent decomposition. The results presented here suggest urea exhibits a slow reactivity rate with nitrite. The relative reactivity rate for sulfamic acid was not assessed, due to its long dissolution time in nitric acid (1 to 2 h). However, the similarity in this reagent's behavior to that of urea (lack of gas evolution, etc.) suggested a reactivity rate similar to that of urea.

Differences in the length of nitrite suppression activity were also noted. Hydrazine, despite its initially rapid reactivity with nitrous acid, exhibited a limited duration for suppression activity. Supernate solutions colored within hours following ascorbic acid addition, indicating a relatively rapid onset of ascorbic acid degradation and reappearance of nitrite in solution. Conversely, despite urea's initially slow onset to reactivity with nitrite, it exhibited nitrite suppression activity for periods exceeding 24 h. Active suppression for up to several days was not uncommon with this reagent. Relative nitrite

suppression activity was based on the time before reappearance of nitrous acid color in solution. Of the reagents added to test solutions, sulfamic acid exhibited the longest nitrite suppression activity; samples submitted for analysis several days following an initial filtration step contained additional silver solid, indicating continued reduction of silver (and hence nitrite suppression activity) in the supernate. The duration of nitrite suppression for hydroxylamine was not assessed.

2.3 CEPOD Anolyte Experiments: Oil Destruction Runs

A series of experiments was performed on an actual waste stream anolyte generated in CEPOD-III (flat plate dissolver design) oil destruction runs (no radioactive contamination). Table 2.2 lists silver recovery results for these experiments. The anolyte was 1 M in HNO_3, and the silver concentration was determined after 30 min of reaction time.

As with nitric acid test solutions, results for CEPOD anolyte samples in Table 2.2 show silver was also successfully recovered to below the waste stream effluent limit of 5 ppm. Data in Table 2.2 also show that addition of a nitrite suppressor enhanced the recovery results. Contamination by extraneous metal ions was high in these samples before silver removal. Table 2.3 lists concentrations for the metal ion contaminants before and after treatment for different nitrite suppressors.

Data in Table 2.3 show that little change occurred in the various metal ion concentrations before or after ascorbic acid addition, as would be expected based on standard electrode reduction potentials. As a check, the extent of contaminant ion adsorption in the silver metal recovered from the CEPOD supernate solutions was determined. Silver metal taken from the various sample vials was washed, filtered, and redissolved in 1 M nitric acid. A mass spectrometry analysis (using an inductively coupled plasma ionization source, ICP-MS) of these samples gave the results shown in Table 2.4. (Only those metals reasonably expected to appear in the silver were checked.) It is apparent from Table 2.4 that contamination of the recovered silver metal is at the part per billion level, except for boron and molybdenum. Even these metals, which were specific to oils treated in this particular CEPOD-III dissolver run, are present at levels less than 5 ppm.

Table 2.2. Effect of Various Nitrite Suppressors on Silver Removal. Silver concentration determined after 30 minutes reaction time.

Supernate Silver Concentration (ppm)[a]			
No Suppressor	Hydrazine	Sulfamic Acid	Urea
1.22 ± 0.09	0.50 ± 0.02	0.68 ± 0.07	0.9 ± 0.3

(a) Silver and ascorbic acid concentrations were 0.02 M and 0.04 M, respectively, in each sample. Error values indicate reproducibility of the measurement, not ICP detection limits.

Table 2.3. Partial Elemental Analysis of Solutions Before and After Silver Removal. Results for various nitrite suppressors (and for no suppressor) are shown.

Metal Ion	Before Ascorbic Acid Addition (ppm)[a]	After Ascorbic Acid Addition (ppm)[a]			
		No Suppressor	Hydrazine	Sulfamic Acid	Urea
Al	50 ± 2	47 ± 1	47 ± 1	47 ± 1	44 ± 3
Ca	22 ± 2	20.8 ± 0.4	20.6 ± 0.7	20.4 ± 0.5	20.5 ± 0.9
Cu	52.4 ± 0.9	50 ± 1	49 ± 2	49 ± 1	49 ± 2
Cr	43.4 ± 0.9	41.4 ± 0.8	41 ± 1	41 ± 1	41 ± 2
Fe	58 ± 1	57 ± 1	56 ± 2	55 ± 1	55 ± 3
Mg	7.3 ± 0.3	7.1 ± 0.2	7.0 ± 0.2	7.0 ± 0.2	7.0 ± 0.3
Ni	148 ± 3	143 ± 2	140 ± 5	140 ± 4	138 ± 6
Zn	36.7 ± 0.4	34.6 ± 0.7	33.9 ± 0.9	33.8 ± 0.7	34 ± 2
Co	6.1 ± 0.0	6.3 ± 0.1	6.1 ± 0.2	6.1 ± 0.2	6.1 ± 0.2
Mn	1.7 ± 0.0	1.60 ± 0.03	1.59 ± 0.05	1.58 ± 0.04	1.57 ± 0.7
Mo	19.5 ± 0.8	14.5 ± 0.2	18 ± 1	17.0 ± 0.6	14 ± 1
Pb	6.4 ± 0.0	6.4 ± 0.1	6.2 ± 0.3	6.2 ± 0.2	6.2 ± 0.3
Ti	28.7 ± 0.4	29.1 ± 0.5	29 ± 1	28.6 ± 0.8	29 ± 2

(a) Error values represent standard deviation for a combination of three repeat samples, not ICP detection limits.

Table 2.4. Partial Elemental Analysis of Recovered Silver Metal. Results for two nitrite suppressors are shown.

Cation	Urea (ppm)[a]	Hydrazine (ppm)[a]	ICP Detection Limit
Ca	0.65 ± 0.44	0.26 ± 0.07	0.1
Cu	0.10 ± 0.02	0.08 ± 0.01	0.01
Zn	0.19 ± 0.11	0.15 ± 0.03	0.05
B	2.63 ± 0.29	2.43 ± 0.16	0.01
Mo	BD[b]	3.92 ± 0.09	0.1

(a) Error values represent standard deviation for repeat experiments. Urea and hydrazine headings indicate silver dissolution results for samples originally containing the given nitrite suppressor reagent.
(b) Below ICP-MS detection limit. All other metals listed in Table 2.4 were below detection limits.

2.4 CEPOD Anolyte Experiments: Plutonium Contaminated Residue Runs

A final series of experiments was performed on a plutonium contaminated rinse solution from a CEPOD-II (cylindrical design) dissolver run. Two samples were prepared from the feedstock solution: one containing original plutonium, the other was plutonium-free after pretreatment through an anion exchange resin (Lewatit UMP-950, Fabrenfabriek Bayer, Germany). Americium and uranium were not removed by this ion exchange. Both solutions were diluted six-fold to a nitric acid concentration of 1 mol/L, giving a plutonium concentration of approximately 16 ppm in the plutonium containing solution. Table 2.5 lists results of the ascorbic acid reduction using different nitrite suppressors for the plutonium and non-plutonium samples.

Data in Table 2.5 show, as expected, a silver recovery to below the 5-ppm target. Unexpectedly, recoveries in the Plutonium-containing samples were better relative to their anion-exchanged counterparts; results show factors from one to five-fold more silver was recovered in the former samples. Although the explanation for this phenomenon is unclear, it may be a consequence of unidentified radiolytic effects.

2.5 Preliminary Conclusions

Results of these preliminary experiments show that silver concentrations may be easily reduced to levels below 5 ppm from CEPOD anolyte solutions by using ascorbic acid. The Ag^+ in solution is reduced to metallic silver, which immediately precipitates and may be filtered out. The effectiveness of the technique, however, is highly dependent on the concentration of H^+ and the presence of nitrite. Lowering the acidity of the solutions (to 2 N or lower in H^+), combined with the use of one of the nitrite suppressors listed in Section 2.1 and an excess of ascorbic acid ensures removal of silver to acceptable levels (< 5 ppm).

Table 2.5. Silver Removal from Radioactive Solutions[a]

	Silver Concentrations (ppm)[b]			
Sample	Hydrazine	Urea	Sulfamic Acid	Hydroxylamine
Pu	0.62	0.64	0.32	0.36
No Pu	2.36	1.32	4.72	1.36

(a) Concentrations for silver and ascorbic acid were 0.01 M and 0.02 M in the test samples, respectively.
(b) These values represent a single measurement only. Detection limit was 0.01 ppm.

This technique successfully removed silver from CEPOD anolyte that had been used for CEPOD processing of radioactive and nonradioactive materials. Although many other metals were present in these solutions, silver alone was reduced to the metal, making separation from the other metal ions and solution species straightforward. Contamination of the recovered silver by other metals was very low (< 5 ppm for any given metal, and < 10 ppm total).

The reactivity of the nitrite suppressors toward nitrite was qualitatively observed to follow the order given in Section 2.1. However, an inverse relationship was observed between the reactivity and the duration of effective nitrite suppression. Hydrazine was most reactive, but gave the shortest nitrite suppression, while urea and sulfamic acid appeared to react most slowly, but gave the longest nitrite suppression. On a per mole basis, the use of hydroxylamine and sulfamic acid resulted in the most effective silver removal over a range of conditions. Because sulfamic acid requires a long dissolution and reaction time, hydroxylamine was chosen for nitrite suppression in most of the subsequent experiments.

3.0 Recent Experiments

3.1 Background

The preliminary experiments described above demonstrate the effectiveness of silver removal from CEPOD solutions by reduction with ascorbic acid. However, demonstration on a larger scale was deemed necessary for the acceptance of this technique. A series of experiments performed for this purpose are discussed below.

Results of the earlier experiments, along with additional bench-scale studies, were used to optimize parameters for removing silver from liter-scale volumes of CEPOD dissolver run solutions. Experiments on the larger volumes were first performed on nonradioactive solutions that had been used to destroy oils, wood, paper, and other materials. Experiments on plutonium contaminated solutions followed.

3.2 Experimental

Ascorbic acid, $C_6H_8O_6$, was used as before to reduce the Ag^+ to metallic silver. Hydroxylamine was the chosen nitrite suppressor for most of the experiments because of its demonstrated effectiveness. Hydrazine was also used in several tests. Urea and sulfamic acid were considered unsuitable because of the long reaction time required before ascorbic acid addition (about 60 min) and long dissolution time (sulfamic acid, 1 to 2 h in nitric acid).

Hydroxylamine sulfate, $(NH_2OH)_2 \bullet H_2SO_4$ (HAS), a crystalline solid, was used as the source of hydroxylamine and was generally added as a 1 M solution to test samples. An 85% solution of hydrazine hydrate ($NH_2NH_2 \bullet 6H_2O$) was used as the hydrazine source. This solution was equivalent to a 17.5 M solution of hydrazine and was added either directly or as a 1 M solution.

A silver sensitive electrode was used to determine silver concentrations in solution. This electrode was paired with a double junction reference electrode. Because the samples were 1 to 2 M in nitric acid, the normal filling solution for the outer reservoir of the reference electrode was 2 M in nitric acid. This concentration provided a satisfactory potential difference (about 50 mV) over the Ag concentration range of 1 to 10 ppm. Silver calibration standards reflected the expected sample solutions of 1 or 2 M in nitric acid and 0.1 M in HAS or hydrazine. (A check of calibration standards with and without nitrite suppressors showed a small but significant difference.) The addition of ascorbic acid to a 2 M nitric acid solution that was 0.1 M in the nitrite suppressors also indicated a small change. The fact that ascorbic cannot be used in the calibration solutions was factored into the error estimates for the concentrations determined with the electrode. Other errors included inaccurate standard solutions and drift in the electrode system.

Initial calibration of the electrode from 0.5 to 50 ppm Ag demonstrated that the log of the silver concentration versus the observed electrode potential was linear over this range (Figure 3.1, open boxes). Tests indicated that the electrode was stable over the course of 2 to 3 h. To minimize errors caused by drift, the electrode was calibrated using standards with silver ion concentrations between 1.08 and 10.8 ppm before each series of measurements. (Measured values between 0.5 and 30 ppm are believed to be accurate to within 1 ppm following calibration with reliable standards.)

After several weeks, the electrode response was rechecked over the larger range (Figure 3.1, filled circles). The same behavior was observed, although the fits had slightly different slopes and intercepts. The noise in the top curve in Figure 3.1 is believed to have been caused by imprecise standard solution preparation. Greater care was taken in subsequent standard preparation, resulting in the much smaller scatter seen in the lower curve. The noise in this curve reflects the nonlinearity of the electrode response over this large range. It is apparent this effect is small even over this range.

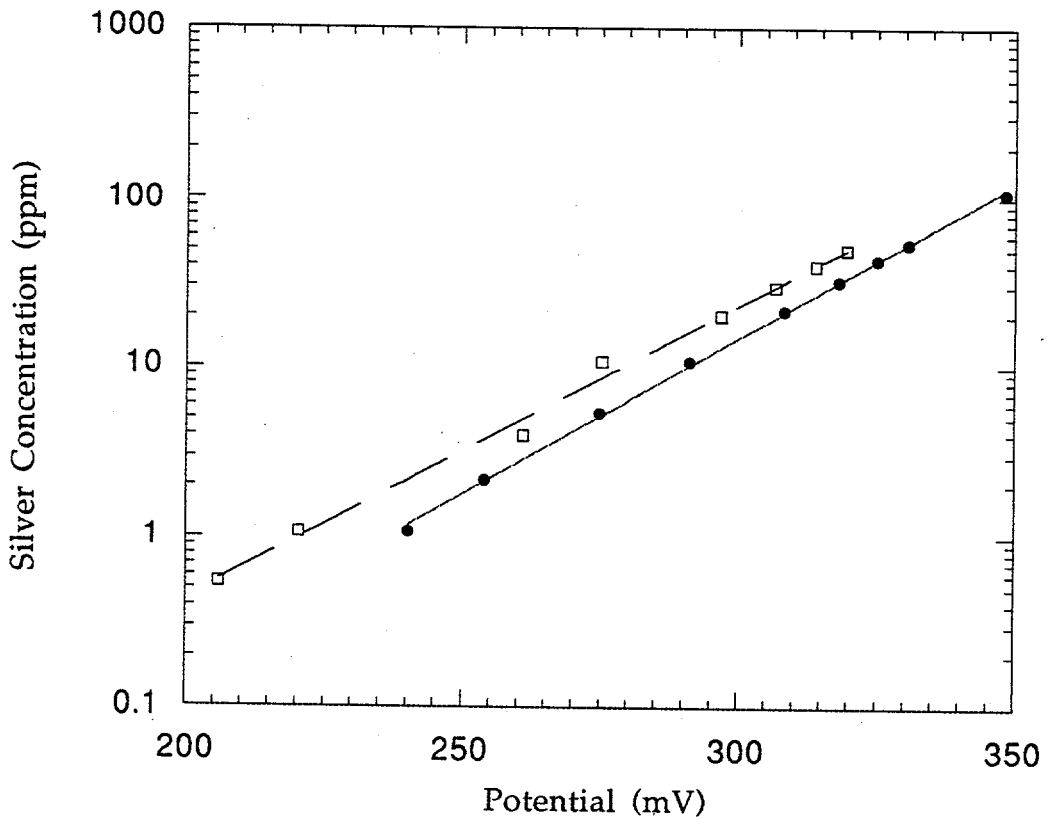


Figure 3.1. Calibration of Silver Sensitive Electrode. Two different calibrations are shown.

Solution masses were determined from densities. The solutions in tanks inside the glove box were stirred by sparging with air. Solutions were added by vacuum transfer from inside (up to 1-L volumes) or outside (larger volumes) the glove box. Silver concentrations were checked using electrodes inside the glove box. Cables from the electrodes were passed through a hole in a transparent plastic port to outside control and measurement electronics. Silicone rubber sealant was used to seal around the cables. Some samples were removed from the glovebox for subsequent analysis using ICP-MS and to determine H^+ concentration.

3.3 Results

3.3.1 Bench-Scale Experiments

Several experiments using small volumes of solution (20 to 30 mL) were performed to optimize parameters not considered in the preliminary experiments. The effectiveness of silver removal as a function of HAS concentration was tested. Solutions 0.1 M in silver nitrate and 1 M in nitric acid were spiked to give initial HAS concentrations of 0.05, 0.10, 0.20, and 0.30 M. (Note that the concentration of hydroxylamine is double that of HAS.) After allowing 15 min for nitrite suppression, the solutions were spiked to make them initially 0.2 M in ascorbic acid. After 60 min, the silver concentration remaining in solution was measured; less than 0.5 ppm remained in each sample. The 0.10 M HAS concentration resulted in slightly greater silver removal than the others, and was therefore used in most subsequent experiments.

The dependence of the extent of silver reduction on the time allowed for reaction of HAS with nitrite was also tested. In this experiment, five solutions (0.1 M in Ag and 1 M in HNO_3), were spiked with 1 M HAS to bring the concentration of the nitrite suppressor to 0.1 M. Ascorbic acid was added to the first solution after 10 min, to the second solution after 15 min, and so on to give HAS reaction times of 10, 15, 20, 40, and 60 min. (Enough was added to make the initial ascorbic acid concentration 0.2 M.) The silver concentration was measured 60 min after the ascorbic acid addition. For the 10- and 15-min HAS reaction times, the concentration of silver ion remaining in solution was 0.3 ppm. For reaction times longer than 15 min, the final silver concentration was slightly higher, but still under 0.7 ppm. In subsequent experiments, a 10- to 15-min reaction time was allowed for nitrite suppression.

The effectiveness of silver removal as a function of acid concentration was then studied using the parameters optimized in the previous experiments. A 0.1 M silver nitrate solution at the appropriate acid concentration was spiked to 0.1 M with HAS, and 15 min was allowed for reaction. The solution was then spiked to 0.2 M in ascorbic acid. After 60 min, the concentration of silver left in solution was measured; results are shown in Table 3.1. For solutions as high as 3 M in nitric acid, recovery to below 5 ppm is possible after 1 h. Removal of silver to less than 5 ppm may be possible even in the 4 M nitric solution given enough time. This possibility was not tested.

Differences in reactivity toward nitrite were qualitatively observed in the preliminary experiments, as noted above. An experiment was performed to determine whether this difference appeared in the rate of silver reduction in the test solutions. A 1 M nitric acid solution was made 0.1 M in silver nitrate and spiked with HAS or hydrazine to a concentration of 0.1 M. Five minutes were allowed

Table 3.1. Silver Removal as a Function of Acid Concentration

Nitric Acid Concentration	Final [Ag] (ppm)
1 M	0.5
2 M	0.8
3 M	2.4
4 M	13

for reaction, then the solution was spiked to 0.2 M with ascorbic acid. The silver concentration was recorded before the ascorbic acid spike and immediately thereafter at short intervals (seconds to minutes depending on the reaction rate). Results are shown in Figure 3.2. When hydrazine was used to suppress nitrite, silver reduction was very rapid. The first two data points, at 15 and 30 s, are beyond the calibration range of the electrode (i.e., above 100 ppm), but indicate a silver ion concentration well above 1,000 ppm. (For comparison, a 0.1 M silver ion solution is 10,800 ppm.) The next point, at 45 s, falls on the plot at roughly 10 ppm. The reduction of silver ion was markedly slower when HAS was used as a nitrite suppressor, as can be seen in Figure 3.2. Plots of the reciprocal of the concentration versus the reaction time display linear regions over roughly one and a half orders of magnitude (Figure 3.3). This suggests that, in this region at least, the reaction is second order in silver ion. The second order rate constants in these regions are 0.002 $s^{-1}ppm^{-1}$ for the HAS run and 0.03 $s^{-1}ppm^{-1}$ for the hydrazine run.

3.3.2 Nonradioactive Process-Scale Experiment

The bench-scale studies reported above were used to choose the optimum parameters for removing silver from larger volumes of spent CEPOD anolyte. The first process-scale test used nonradioactive CEPOD anolyte that originated from a CEPOD dissolver run used to destroy oil, paper, and other materials. An atomic absorption analyzer with an inductively coupled plasma ionization source (ICP AA) indicated about 9.918 g/L silver was present (about 0.09 M), with much lower quantities of Fe, Ce, and other elements. The solution was found (by dilution and pH measurement) to be slightly less than 2.5 M in nitric acid.

A 6-L batch of this solution (Batch 1) was placed in a 15-L polyethylene carboy. Distilled water (3 L) and HAS (1 L, 1.2 M) were added with stirring to make 10 L of solution. After 15 min, 2 L of a 1.2 M ascorbic acid solution was added to make a total of 12 L of solution. The solution turned brownish-yellow, and silver began to precipitate immediately. The "initial" concentrations in this final 12 L were 0.10 M HAS (0.20 M hydroxylamine), 0.20 M ascorbic acid, 0.05 M Ag^+, and 1.25 M H^+. After 2.5 h, 30 mL of the solution was filtered (0.2 μm), and the silver concentration checked with the silver sensitive electrode. (This was recalibrated immediately before measurement.) The silver in solution was reduced to 0.6 ppm. This excellent removal is not surprising given the ratio of HAS and ascorbic acid to silver ion (approx 4:4:1) and the long reaction time that was allowed. A summary of the processing is shown in Table 3.2.

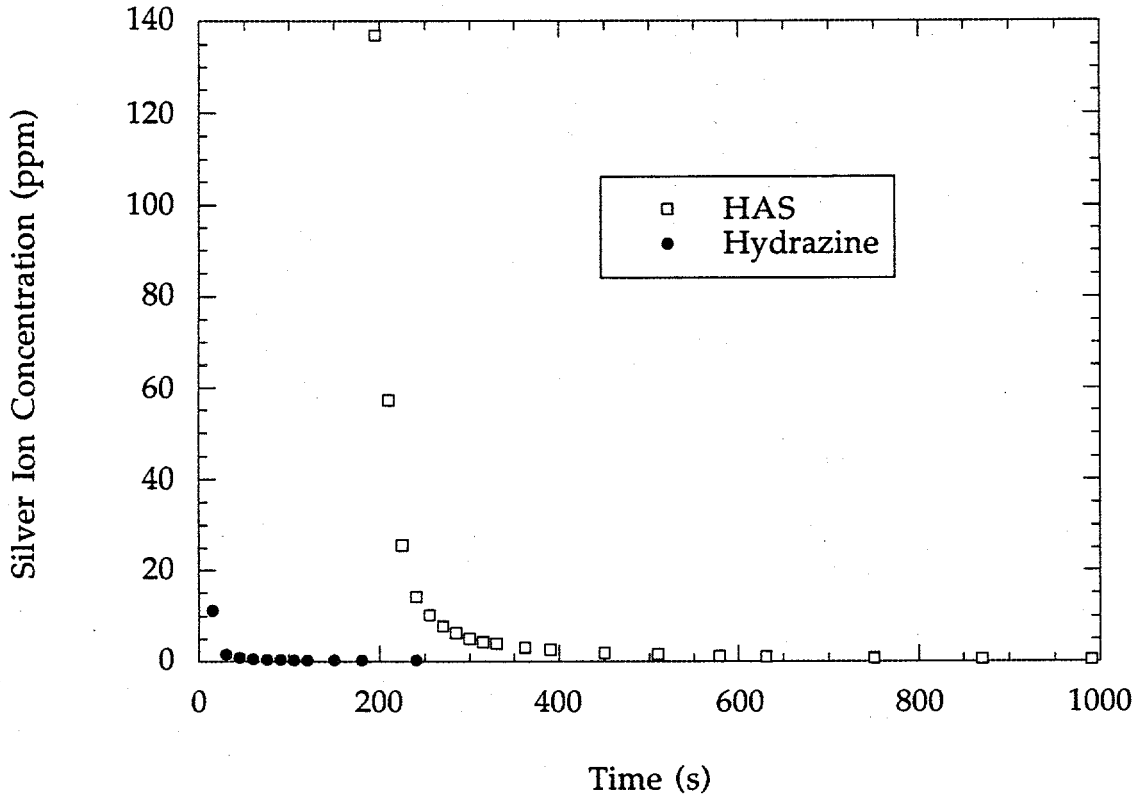


Figure 3.2. Silver Ion Removal Rate. Silver concentration in solution is plotted as a function of time after ascorbic acid addition. Solid circles (open squares) show run in which hydrazine (HAS) was used for nitrite suppression.

3.3.3 Radioactive Process-Scale Experiment

Recovery of silver from radioactive CEPOD anolyte was attempted next. The first effort to do so was not successful due to the presence of chloride ion in solution. Because AgCl displays a significant solubility (~1.8 ppm in water at 25°C, 5.2 ppm at 50°C), enough ascorbic acid was added to reduce all the silver (both in solution and in AgCl) to metal. Silver appeared to precipitate readily. After 1 h of vigorous sparging, the tank was sampled, and the silver concentration was found to be about 100 ppm. Subsequent sparging and ascorbic acid additions lowered the levels of silver in solution, but not to the acceptable 5 ppm concentration. The difficulties encountered demonstrate the importance of ensuring the CEPOD anolyte is free of chloride before silver removal.

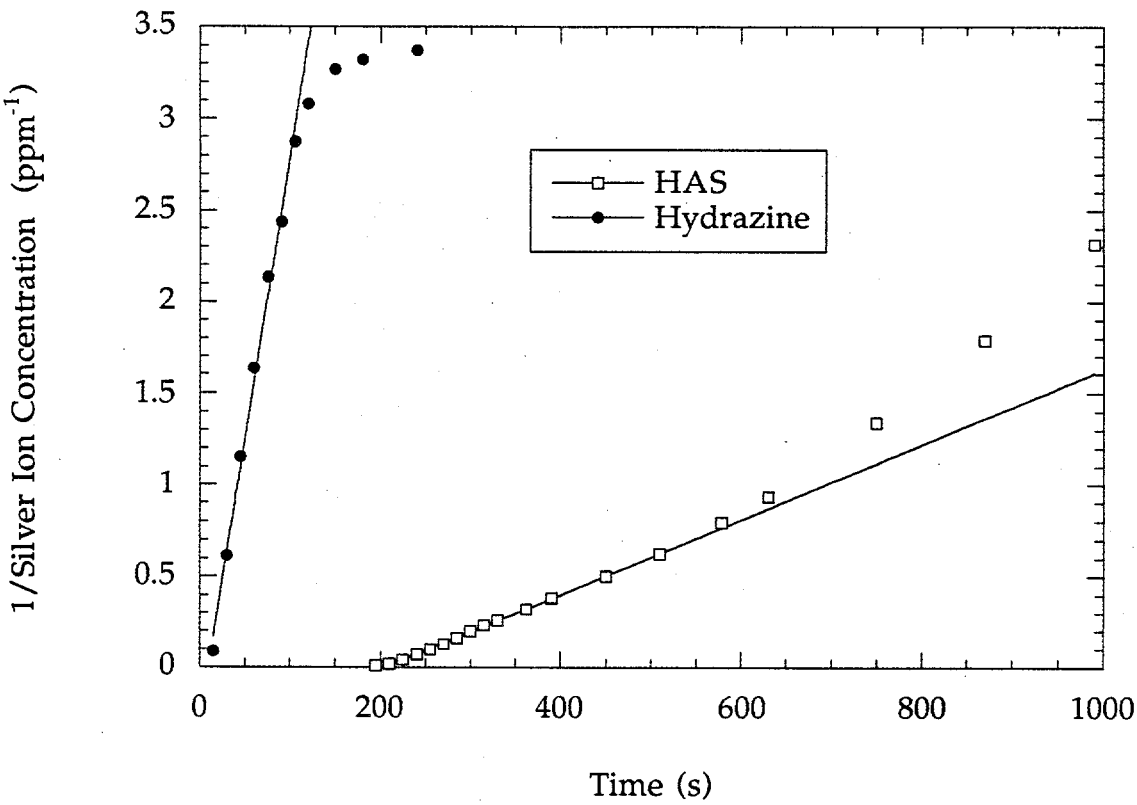


Figure 3.3. Silver Ion Removal Kinetics. The reciprocal of the silver concentration is plotted versus time after ascorbic acid addition. The lines are fits to the data in the linear region and give second order rate constants of 0.002 s^{-1} ppm^{-1} (HAS, open squares) and 0.03 s^{-1} ppm^{-1} (hydrazine, filled circles).

Table 3.2. Batch 1 Processing Summary: Nonradioactive CEPOD Anolyte

Reagent Added	Total Vol/Mass	Reagent Concentration	Ag^+ Concentration
Batch 1	6 L/6.8 kg	-----	0.10 M
Water, HAS	10L/11kg[a]	0.12 M	0.06 M[a]
Water, Ascorbic Acid	12 L/13.4 kg[a]	0.20 M	0.6 ppm

(a) The two masses and the noted concentration were estimated.

Two successful efforts followed. CEPOD anolyte from a dissolver run was used. This clear, light green solution was found to contain 0.27 M of silver ion and 51 mg/L of ^{239}Pu. Americium and other plutonium isotopes are expected to be the other major radioactive contaminants present, but at levels below 5 mg/L. A 2-L batch of this solution (Batch 2) was placed in a 30-L glass processing tank in a glove box. Distilled water (2 L) and HAS (0.25 L, 2 M) were added to make 4.25 L of solution. After sparging 15 min, 0.5 L of a 2 M ascorbic acid slurry was added for a total of 4.75 L of solution. Silver began to precipitate immediately. The "initial" concentrations in this final 4.75 L were 0.10 M HAS (0.20 M hydroxylamine), 0.21 M ascorbic acid, and 0.11 M Ag^+. The H^+ concentration was not checked, but was expected to be 2.5 N in the original 2-L of solution. After 1.5 h, 30 mL of the solution was filtered (0.2 μm), and the silver concentration was measured with the silver sensitive electrode, which was recalibrated immediately before measurement. The silver in solution was reduced to less than 0.5 ppm. Compared to the previous (nonradioactive) batch, less nitrite suppressor and ascorbic acid were used relative to silver (approximately 2:2:1), and the reaction time was shorter. Results were still excellent, with silver removed to levels far below the 5 ppm limit. A processing summary is given in Table 3.3.

The silver ion was also removed from a third and final batch of CEPOD anolyte. Five and one half liters of CEPOD anolyte from a dissolver run was again used. (A sample was removed for ICP-MS analysis of the silver and ^{239}Pu concentrations. They were 0.25 M and 240 mg/L, respectively. Americium and other plutonium isotopes are again expected to be the other major radioactive contaminants present at levels below 5 mg/L. The H^+ concentration of this sample was found to be 2.5 N.) Distilled water (4.25 L) and HAS (0.25 L, 2 M) were added to make 9.5 L of solution. After sparging 20 min, 0.6 L of a 2 M ascorbic acid slurry was added for a total of 10.1 L of solution. Silver again began to precipitate immediately. The "initial" concentrations in this 10.1 L were 0.05 M HAS (0.10 M hydroxylamine), 0.12 M ascorbic acid, and 0.14 M Ag^+. After sparging for 1.5 h, the solution was sampled.

The silver concentration was measured with the silver sensitive electrode (after recalibration) and found to be 0.6 ppm, again falling below the maximum RCRA limit. A sample was also removed for later ICP-MS analysis. This analysis confirmed the silver concentration (0.6 ppm $\pm$ 10%). The plutonium concentration was slightly less than expected for the dilution (112 ppm found versus 131.5 ppm expected). The reason for this discrepancy is unknown. The concentration of H^+ in the

Table 3.3. Batch 2 and 3 Processing Summary: Radioactive CEPOD Anolyte

Reagent Added	Total Vol./Mass (L/kg)	Reagent Concentration (M)	H^+ Concentration (N)	Ag^+ Concentration	Ag^0 Mass (kg)
Batch 2	2.0/2.3	–	–	0.27 M	–
Water, HAS	4.3/4.4	0.12	–	0.12 M[a]	–
Water, Ascorbic Acid	4.8/5.3	0.20	–	0.4 ppm	0.057[a]
Batch 3	5.5/6.2	–	2.5	0.25 M	–
Water, HAS	9.5/10	0.05	–	0.14 M[a]	–
Water, Asc	10.1/11	0.12	1.9	0.6 ppm	0.147[a]

(a) Estimated. The total mass, 0.198 kg, was determined as noted in the text.

final solution was found to be 1.9 N. The concentrations of the nitrite suppressor and the ascorbic acid were again reduced relative to silver (~ 1:1:1), again with excellent results. The processing summary for this batch is included in Table 3.3.

Batches 2 and 3 were vacuum filtered (12 μm) to remove the solid silver metal. Three filters were required, and filter mass was determined before and after filtering. (All solids were assumed to be silver, since the preliminary study indicated very little contamination of recovered metal in this process.) A total of 198 g of silver was recovered. There was an insignificant amount of silver in the final solutions (8 mg). The feed solutions contained a total of 204 g of silver, indicating a loss of 6 g of solids, or 3%. Most of this loss probably occurred during a filter change in which the loaded filter was actually overloaded with solids. For this reason, the recovery of the solid silver can likely be improved. A mass balance for the silver is given in Table 3.4.

Batches 2 and 3 had solution process times (i.e., time from addition of the first reagent until the check for solution silver) of approximately 2 h. The bulk of this time was required for nitrite suppression (20 min) and ascorbic acid reduction (1.5 h). Judging by the results of the bench-scale studies (Section 3.3.1), this time could probably be reduced to 45 min or less and still produce the desired reduction of solution silver (<5 ppm).

Table 3.4. Material Balance for Silver Recovery Runs

Initial Silver Balance	Calculations	
Batch 2	2.0 L x 0.266 M x 107.868 g/mol =	57 g
Batch 3	5.5 L x 0.247 M x 107.868 g/mol =	147 g
Total		204 g
Final Silver Balance		
Filter 1	123.07 g - 98.51 g =	24.56 g
Filter 2	241.87 g - 99.07 g =	142.80 g
Filter 3	131.43 g - 100.77 g =	30.66 g
Total		198.02 g
Batch 2	4.75 L x 0.4 mg/L =	1.7 mg
Batch 3	10.1 L x 0.6 mg/L =	6.1 mg
Total		7.8 mg
Total		198.03 g
Difference		
Unaccounted Silver	6 g	
Percent Loss	3%	

3.4 Discussion

The use of HAS to suppress nitrite resulted in rapid and nearly complete silver reduction. This reagent was chosen to strike a balance between the speed (i.e., reactivity) and the duration of nitrite suppression. (Continued suppression of nitrite is important if the precipitated silver cannot be immediately separated from the solution. Without nitrite suppression, the ascorbic acid is oxidized by reformed nitrite and can no longer prevent redissolution of silver metal by the acid. Hydroxylamine appeared to suppress nitrite over a period of tens of hours, although quantitative measurements were not taken.) The use of other hydroxylamine salts may prove similarly effective for nitrite suppression and may provide other benefits. Hydroxylamine nitrate (HAN, $NH_2OH \bullet HNO_3$), for instance, may be a good choice if the exclusion of sulfate from the waste stream is desirable. Hydroxylamine nitrate is commercially available as a 24% aqueous solution, which provides ease of mixing with other solutions. On the other hand, liquids may present transportation safety concerns that do not apply to solids such as HAS.

Any form of hydroxylamine is probably a better choice than hydrazine from a processing standpoint. Hydrazine is more reactive, more toxic, and under the right conditions may form potentially explosive azide salts by the following sequence of reactions (Cotton and Wilkinson 1988):

$$N_2H_{4(aq)} + H_3O^+_{(aq)} = N_2H^+_{5(aq)} + H_2O \tag{3.1}$$

$$N_2H^+_{5(aq)} + HNO_{2(aq)} = HN_{3(aq)} + H^+_{(aq)} + 2H_2O \tag{3.2}$$

$$HN_{3(aq)} + Ag^+ = AgN_3 \downarrow + H^+_{(aq)} \tag{3.3}$$

On the basis of the process-scale experiments to remove silver from CEPOD solutions, a generic flowsheet was developed (Figure 3.4). Because silver reduction was observed to proceed most rapidly and completely at lower acid concentrations, the feed solution is shown as significantly diluted during nitrite suppressor (N.S.) and ascorbic acid (Asc.) addition. Because dilution will increase the final waste stream volume, less dilution may be desirable. Silver removal to levels below 5 ppm was demonstrated in this study for acid concentrations as high as 3 M (hydroxylamine) and 4 M (sulfamic acid). The removal of silver from solutions 4 M in nitric acid may be possible, provided greater concentrations of nitrite suppressor and ascorbic acid relative to silver ion, and/or longer reaction times, are used, which would reduce or remove the need for dilution.

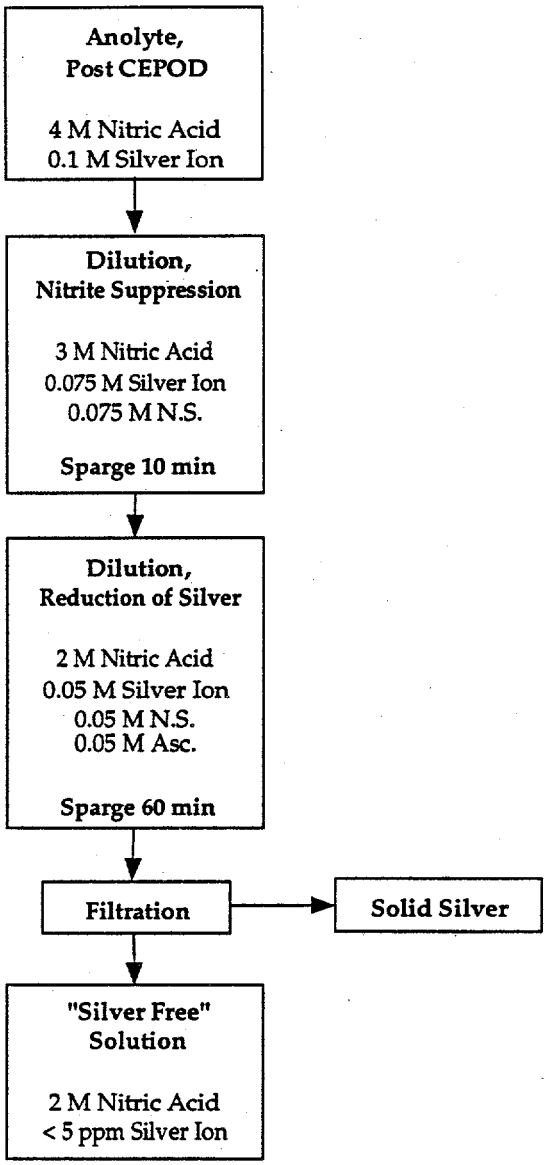


Figure 3.4. Conceptual Processing Flowsheet for Silver Removal. "N.S." indicates a nitrite suppressor, "Asc." indicates ascorbic acid.

Another group[a] demonstrated the removal of silver from acid solutions by an alternate method, electro-deposition. In this procedure, the silver is deposited on a platinum screen or reticulated vitreous carbon (RVC) cathode by passing current through the solution from a platinum anode while maintaining the cell potential slightly higher than necessary to convert Ag^+ to silver metal. The silver concentration in a 4 M nitric acid solution was reduced from 0.5 M to 6 ppm in 3 h using a 1 A current and a Pt screen with a surface area of 103.1 cm^2. The solution was held at 10°C, and the experiment was run under stationary conditions (i.e., mixing, but no recirculation of the solution). Due to the solubility of Ag in nitric acid, higher acid concentration slowed silver removal. For example, in 6 M nitric acid, the silver concentration was reduced from 0.5 M to only 10,986 ppm (0.1 M) in 3 h. The process was also less effective at ambient temperature: at 25°C, the silver was only reduced to 8,179 ppm in 2.5 h (compared to approximately 100 ppm in the same time for the first run described above.)

Silver removal was also attempted using RVC electrodes in both stationary and recycle flow reactors. Although the reduction of silver from 0.5 M to the 1,000-ppm range was demonstrated in a recycle flow reactor, conditions were not found in which the silver concentration could be reduced from 0.5 M to below 5 ppm. (The lowest concentration attained when starting with 0.5 M was 874 ppm.) However, a recycle flow reactor that employed the RVC electrodes effectively removed lower concentrations of silver. The silver concentration in a 4 M nitric acid solution was reduced from 0.03 M to 0.5 ppm in 4 h, and from 0.02 M to below 0.5 ppm in 3 h using an RVC electrode with a total area of about 93 cm^2. The current was 0.4 A, and the solution was again held at 10°C. These results suggest that an optimized process would use two cells: one to remove about 98% of the silver, and another to take this output and reduce the silver concentration to below the discharge limit.

Electro-deposition has the advantage of being easy to use with a CEPOD system, since much of the necessary equipment would be in place for CEPOD processing. However, it appears that a second stage would be necessary, which would add complexity to the system. Also, under the conditions given, the removal of silver by ascorbic acid reduction is much faster (see Figure 3.2). It must be stressed that the electro-deposition results are preliminary, and optimization will bring improvements. Electro-deposition from larger volumes and more complicated solutions, such as those presented in this study, along with a determination of the power required per gram of silver removed and the dependence of this value on the electrode surface area, would provide a better basis for comparing the two methods. A direct cost comparison would also require a consideration of the engineering of appropriate plants which incorporated the two different recovery schemes. At present, however, it is clear that silver may be easily removed by either method.

(a) K. Nobe, M. Schwartz, R. Perez, M. Flamberg, J. Klein, J. Chavez, and R. Hickman, 1992, unpublished results.

4.0 Conclusions

Silver removal from CEPOD solutions to concentrations below the RCRA limit of 5 ppm was demonstrated. Ascorbic acid was used to reduce silver ion to metallic silver, which immediately precipitates from the nitric acid solution. The presence of nitrite (nitrous acid) inhibits the reduction of silver by oxidizing ascorbic acid. Several reagents were tested in bench-scale studies for their effectiveness at suppressing nitrite. The sulfate salt of hydroxylamine was found to be very effective, and was preferred in this study over other reagents because of its ease of use, lower toxicity, and absence of potentially troublesome side reactions. Bench scale studies were also used to optimize other parameters, such as concentrations of reagents and length of nitrite suppressor reaction time. Only trace (ppb) quantities of contaminant metals were found in the recovered silver metal in these studies.

Results from the bench studies were used to engineer silver removal from process-scale volumes (liters) of CEPOD solution. Six liters of anolyte from a CEPOD organic destruction run (nonradioactive) and 7 L of anolyte from a CEPOD plutonium oxide dissolution run (radioactive) were used as feed solution. In all cases (three batches) silver was removed to 0.6 ppm or less, far below the RCRA limit of 5 ppm. A molar ratio as low as 1:1:1, suppressor to ascorbic acid to silver, was used. The solid silver was recovered by filtering. It is believed that the time necessary for the process (from first addition of reagents to reduction of solution silver to <5 ppm) is 45 min or less. Removing silver from CEPOD solutions is easily and effectively accomplished. Thus, the presence of silver in the CEPOD process does not impair its utility as a waste treatment alternative.

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