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UREX Process

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Submitted to: Accelerator Transmutation of Waste Program Office



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**Technetium and Iodine Separations in the
UREX Process**
LAUR-

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**Accelerator Transmutation of Waste Program
Final Report for WBS 1.24.01.01**

Introduction

The Accelerator Transmutation of Waste (ATW) program is being developed to determine the feasibility of separating and transmutating the transactinides (Pu-Cm) and long-lived fission product (^{99}Tc and ^{129}I) from spent light water reactor (LWR) fuel. This approach would help with the disposal of spent commercial fuel. In addition, since the residual waste after ATW treatment will have much lower levels of long-lived species, this process may improve the performance and acceptability of long-term geologic disposal of nuclear waste. A roadmap for the Accelerator Transmutation of Waste (ATW) was submitted to Congress in 1999.¹ This document gave an overall view of the ATW concept and program. A subsequent document prepared by the Technical Working Group for ATW Separations Technologies and Waste Forms issued a second roadmap that dealt more specifically with the radionuclide separations and waste disposal needs for the ATW program.² This latter document discusses the UREX (Uranium Extraction) process. The latest iteration of the UREX flowsheet is shown in Figure 1.³ This flowsheet anticipates the co-extraction of technetium with uranium from dissolved LWR fuel by tributylphosphate (TBP) and their subsequent sequential back-extraction from the TBP stream. The goals of the UREX process are:

1. To separate >99.9% of the uranium from the spent fuel and convert it into a clean product that qualifies as a Class C Waste.
2. To recover >95% of the technetium and iodine so that each element can be formulated into a target for transmutation into stable ruthenium and xenon isotopes, respectively.
3. To keep all the transuranics elements (Pu-Cm) in the raffinate.

The UREX process flowsheet is given in Figure 1. Iodine is not shown in the Figure 1 flowsheet because it will be removed during the LWR fuel dissolution and feed preparation steps. Separation iodine prior to UREX will prevent this element from fractionating into every process stream and from reacting with the UREX organic extractant (30%TBP in dodecane). Experiments need to be performed to optimize the removal and separation of iodine from the dissolved fuel before it enters the UREX process.

This report is divided into two parts: Part 1 deals with the behavior of technetium in the UREX process and Part 2 deals with the conditions for the recovery of iodine during dissolution of spent fuel

Technetium

Chemically, the UREX process is a modification of the PUREX extraction process that has used TBP to extract uranium and plutonium from the nitric acid dissolved spent fuels. For non-proliferation reasons, it is a requirement of UREX that plutonium not be extracted or partitioned in this process; plutonium should always report to the raffinate with the other transuranics and fission products. Thus UREX needs to incorporate aspects of PUREX 2nd cycle Pu/U partitioning into a 1st cycle PUREX extraction procedure. The judicious use of an appropriate reductant will allow this chemistry to proceed as planned.

In order for the selective reduction to take place, plutonium needs to be in and remain in the positive three-oxidation state during the TBP extraction and scrub. A

number of reductants have been used or proposed for this job including ferrous sulfamate⁴, U(IV)⁴, hydroxylamine nitrate⁴, butylaldehyde⁵, isobutylaldehyde⁵, and acetohydroxamic acid (AHA)⁶. Hydrazine (N₂H₄) is often used in conjunction with some of these reductants to reduce nitrite to N₂⁴. This is necessary to prevent the reoxidation of Pu(III) to extractable Pu(IV) by nitrite. Ferrous sulfamate, which has been used in PUREX processing in the past, is discouraged because it adds to the waste volume. U(IV) has been studied over the last 30 years. The U(IV) would not add to the waste volume since it would be generated from the uranium in the spent LWR fuel and would eventually end up in the final uranium waste product. Another advantage of the U(IV) reductant is that it reduces neptunium to the non-extractable five-oxidation state; it simplifies the flowsheet and subsequent processing if neptunium follows Pu(III) into the raffinate. The affect of U(IV) on the redox chemistry of technetium would need to be investigated especially when the co-reductant hydrazine is present. This is especially important since pertechnetate catalyzes the destruction of hydrazine.⁷ Maintaining U(IV) at the large volumes required for LWR processing could present problems. Hanford has apparently also run just HAN by itself. Use of HAN needs to be verified since it is not an effective plutonium reductant above 1 M HNO₃. Recently butylaldehyde has been suggested as a reductant for Pu⁴⁺.⁵ Isobutylaldehyde is even better because it reduces both plutonium and neptunium to non-extractable oxidation states, Pu³⁺ and NpO₂⁺.⁵ Since formaldehyde is a reductant for pertechnetate the effect of these aldehydes would need investigation. The oxidized aldehyde products are the corresponding carboxylic acids thus they could be removed from TBP by a solvent recycle Na₂CO₃ wash.

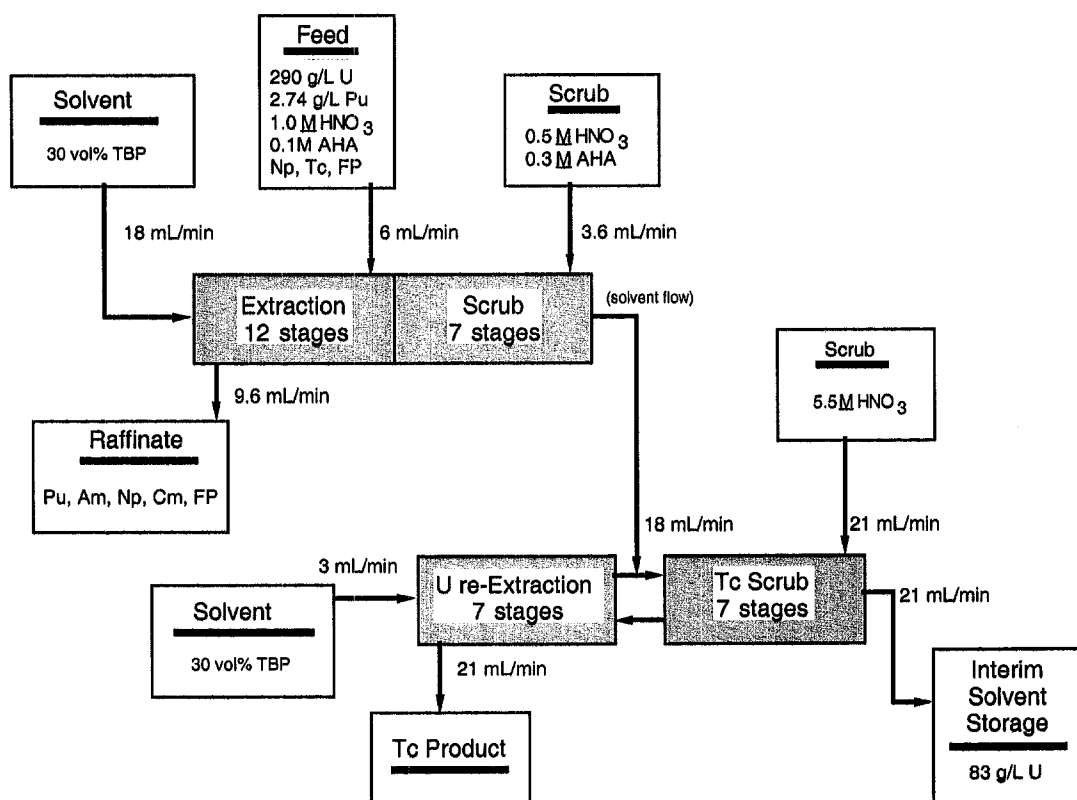
Acetohydroxamic acid (AHA) is being considered as the reductant of choice for the UREX process⁶ because it 1) can reduce Np(VI) to Np (V) quickly, 2) can reduce Pu(IV) to Pu (III) slowly (this reaction is catalyzed by UO₂²⁺), 3) can complex Pu(IV) and Np(IV), 4) is a non residual reductant, and 5) has a growing data base on its potential use in fuel processing. These characteristics will allow UO₂²⁺ to be extracted free of transactinides and thereby avert the partitioning of plutonium. The UO₂²⁺, if it is free of technetium can then be converted to a Class C waste for disposal. The behavior of technetium in UREX/AHA system needs to be studied to determine how well technetium partitions in the process and then determine how to separate and purify it for transmutation.

Iodine

Because of its volatile nature, the control of fission produced iodine has been a major concern to fuel reprocessing facilities and to the general handling and operation of reactor facilities. Two isotopes are of major importance: ¹³¹I and ¹²⁹I. Iodine-131 is short lived (t_{1/2} = 8 days). The longer lived isotope, ¹²⁹I (t_{1/2} = 1.57 x10⁷ years), is of major concern because it impacts the long-term risk assessment associated with the geologic storage of spent nuclear fuels.

It has been known for many years that the radio-iodine vapors released during the dissolution and processing of spent fuels had to be managed carefully. Because I₂ is readily produced in strong nitric acid solutions, the optimum points to separate iodine are during the fuel dissolution and feed preparation steps that occurs prior to the UREX process. Although most of the iodine is expected to be removed during dissolution it is imperative that methods be developed that will ensure that no iodine enters UREX processing streams. This work studies the effective removal of iodine from the feed solution prior to its entry into this process. Since the amount of iodine left after fuel

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HOOD OPERATION:

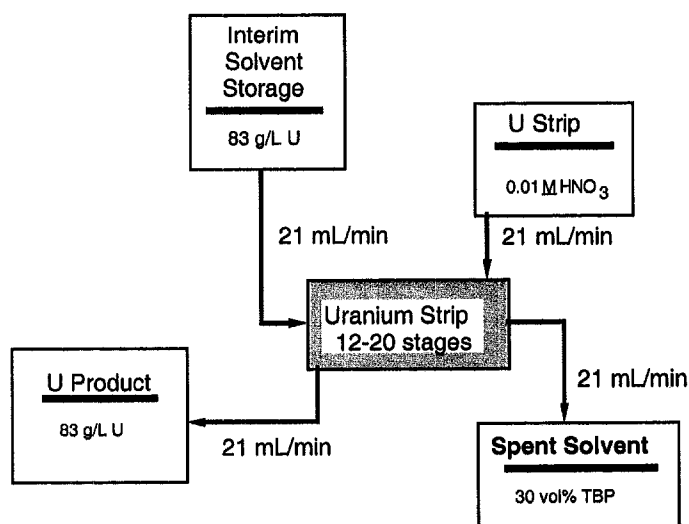


Figure 1. The UREX Process Flowsheet as of June 1, 2001.

dissolution may be variable, the goals for this project are to be able to remove and recover >95% of the iodine from the feed solution. Simulated feed solutions were sparged with nitrogen gas to transport iodine to sodium hydroxide solution traps. The efficiency of this process was studied as a function of temperature, nitrogen flow rate, nitric acid concentration, iodine concentration, solution ionic strength and time. An experimental design approach was used to maximize the efficiency of data collection and economize the number of trials required.

Part 1. Behavior of Technetium in the UREX Process

Technetium will be present as pertechnetate (TcO_4^-) in the feed entering the UREX process. This form of technetium co-extracts with uranium into TBP as the $\text{UO}_2(\text{NO}_3)(\text{TcO}_4) \cdot 2\text{TBP}$.^{8,9} The fundamental questions that need to be answered about technetium in the UREX Process are:

- Does AHA reduce TcO_4^- to a non-extractable form such as TcO^{2+} or to a non-extractable AHA Tc(V) or Tc(IV) complex?
- If reduction occurs, how will technetium be separated from the raffinate?
- If no reduction occurs, how does AHA affect the extraction and stripping of TcO_4^- ?
- Can >95% of the technetium present in dissolved spent fuel be recovered from the UREX process?

The standard reduction potentials for AHA, pertechnetate and some other important couples relevant to the UREX process are shown in Table 1. Depending on the solution matrix the working AHA couple could range between 0.75 and 0.79 volts.^{10,11} Thus the relative order of the AHA and the $\text{TcO}_4^-/\text{TcO}_2$ couples could change leading to a reduction of pertechnetate. Studies were done to determine if pertechnetate could be reduced under the UREX processing conditions.

Table 1. Standard Reduction Potentials of Important Species in the UREX Process.

| Reduction Reaction | | | | | | | | Volts |
|--------------------------------|---|---------------------|---|-----------------------------------|-------------------------------|------------------------|---------------------|-------|
| NpO ₂ ²⁺ | + | e ⁻ | | -----> | NpO ₂ ⁺ | | 1.24 | |
| Pu ⁴⁺ | + | e ⁻ | | -----> | Pu ³⁺ | | 1.01 | |
| NpO ₂ ²⁺ | + | 4H ⁺ | + | 2e ⁻ | -----> | Np ⁴⁺ | + 2H ₂ O | 0.94 |
| Pd ²⁺ | + | 2e ⁻ | | -----> | Pd | | 0.95 | |
| CH ₃ COOH | + | HN(OH) ₂ | + | 2H ⁺ + 2e ⁻ | -----> | CH ₃ CONHOH | + 2H ₂ O | ~0.8 |
| TcO ₄ ⁻ | + | 4H ⁺ | + | 3e ⁻ | -----> | TcO ₂ | + 2H ₂ O | 0.78 |
| Fe ³⁺ | + | e ⁻ | | -----> | Fe ²⁺ | | 0.77 | |
| UO ₂ ²⁺ | + | 4H ⁺ | + | 2e ⁻ | -----> | U ⁴⁺ | + 2H ₂ O | 0.33 |

Experimental: Chemical reagents were obtained from Aldrich, Fisher, and Strem. Ammonium pertechnetate (^{99}Tc) was obtained as from Oak Ridge National Laboratory. This material, which should be white, was black indicating that it had auto-reduced. The oxidation procedures and preparation of the stock pertechnetate solution from this material and the preparation of a stock $^{95\text{m}}\text{NaTcO}_4$ solutions have been reported.¹²⁻¹⁹ The details of the NaI (γ) counting of $^{95\text{m}}\text{Tc}$ and liquid scintillation counting (LSC) of ^{99}Tc and ^{238}U have been described.¹²⁻¹⁹ A stock solution of 30% TBP in dodecane was used. The TBP solution was not pre-contacted with any solution (i.e., carbonate or nitric acid) before being used. Aqueous solutions of pertechnetate in the desired matrix (i.e., HNO_3 solutions, $\text{HNO}_3/\text{UO}_2^{2+}$ solutions, and an LWR simulant solution) were prepared. The LWR simulant was prepared from the oxide or nitrate salts of the desired components. The TcO_4^- concentration ranged between $1\text{--}1.5 \times 10^{-4}$ M. Distribution coefficients (i.e., D_{Tc} , Organic/Aqueous (O/A)) for the extraction were performed by contacting the

aqueous solution with the TBP solution, centrifuging, separating phases and taking 100 μL aliquots for counting. If a reductant was added to the aqueous phase it was usually allowed to sit 1 hour at 25°C, 40°C, 60°C or 90°C before contacting it with the TBP solution at 25°C. Some contacts were done immediately after adding the reductant. AHA concentrations ranged between 0.01 and 0.10 M. Other reductants used ranged between 0.02 and 1.0 M. The concentration of HNO_3 in all the matrixes studied ranged between 0.1-6.0 M. The concentrations of UO_2^{2+} ranged between 0.62-1.7 M. An organic to aqueous phase ratio (O/A) of 1 was used in most studies. Test of the Figure 1 flowsheet used the approximate phase ratios shown in the figure. The TBP solution was not pre-contacted with any solution (i.e., carbonate of nitric acid) before being used. Subsequent scrub and strip contacts were done immediately after the extraction contact.

Uranium concentrations, in either phase, were obtained by adding 100 μL of the sample to 25 ml of water, shaking, and then the sample allowed to settle. All the uranium from the organic phase being measured should be back extracted into the aqueous phase because of the favorable pH (slightly acidic) and phase ratio (O/A= 0.005). The estimated amount uranium extracted into the water phase is >99%. A 1-mL aliquot was withdrawn from below the surface of the liquid. This insures that no organic material from the TBP samples is withdrawn. The aliquot is mixed with 1 mL of 0.5 M sodium salicyclate and the absorbance at 438 nm measured. The standard curve for this method is shown in Figure 2. The method is an adaptation of Muller's method.²⁰ Uranium D_U values were obtained by ratioing the organic phase to aqueous phase absorbance measurements. Absorbance measurements were made with an Ocean Optics, Inc. SD2000 UV-VIS spectrophotometer using 1-cm cells.

Results and Discussion: Table 2 shows the results of various reductants, including AHA, on the extraction of pertechnetate from a simple nitric acid solution. All of these reductants have been used or proposed for use in second cycle PUREX processing to reduce Pu^{4+} to Pu^{3+} so that it can be stripped from the organic phase. Use of ferrous sulfamate is discouraged because it adds to the waste volume. The other reductants are preferable because they are non-residual; that is they can be converted to gaseous product at the end of their use. Hydrazine (N_2H_4) is often used in conjunction with some reductants to reduce nitrite to N_2 . Since hydrazine is a known reductant of pertechnetate it was necessary to test this reagent. Comparing the distribution coefficients for the top five reductants samples to the control sample, which had no reductant, it is obvious that none of the reductants reduced pertechnetate either immediately or after allowing the reductant to react with pertechnetate for one hour. The hydrazine check sample D_{Tc} value shows what the magnitude of the distribution coefficient would be if pertechnetate were reduced. What is interesting about the hydrazine result is that it did not precipitate Tc as the metal or TcO_2 ; thus a soluble reduced technetium species must have been formed that is not extracted by TBP.

Since AHA is the reductant of choice for UREX it was necessary to determine if other experimental conditions would allow pertechnetate to be reduced. Table 3 shows the affect of different nitric acid concentrations on the reduction/extraction of pertechnetate. Comparison of the "No AHA" added sample to the "AHA samples" shows no reduction even if one hour is allowed for the reduction to occur. A check sample using hydrazine as a reductant shows a definite conversion of pertechnetate to a soluble reduced technetium species that does not extract into TBP. Pruett has studied the extraction of pertechnetate from nitric acid solutions.⁹ His data for the four nitric acid

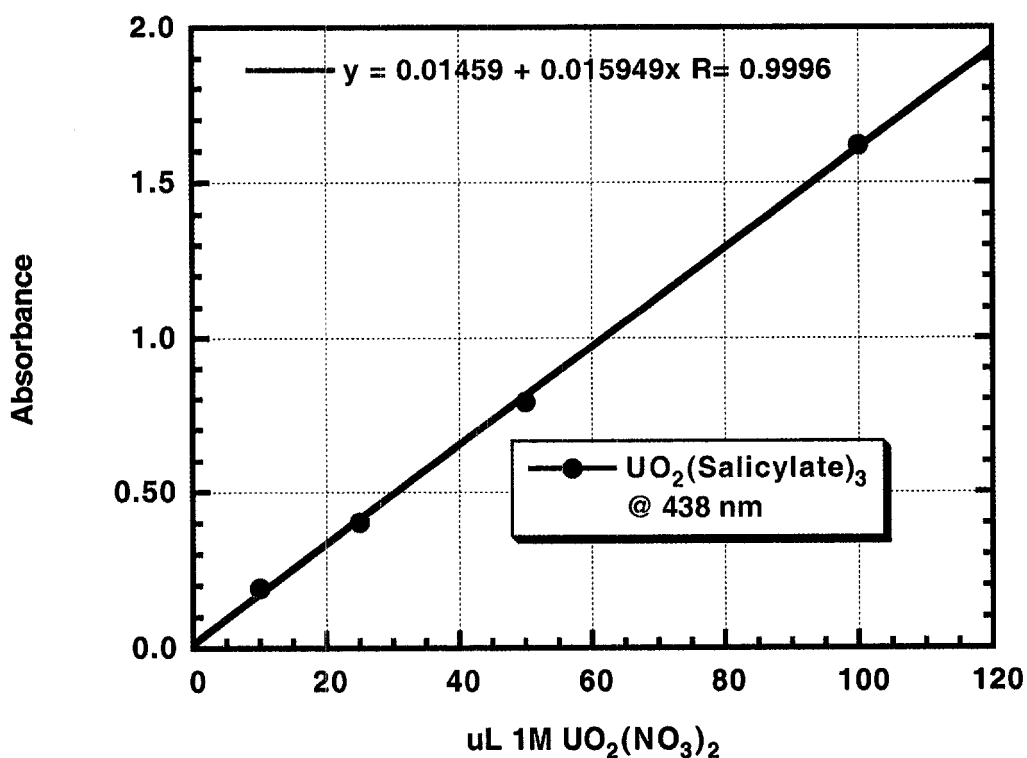


Figure 2. Standard Spectrophotometric Curve for the Measurement of Uranium.

Table 2. Effect of Various Reductants on the TBP (30% in Dodecane) Extraction of TcO₄⁻ (1 x 10⁻⁴ M) from 1 M HNO₃.

| Reductant (0.05 M) | Immediate Contact D _{Tc} (o/a) | 1 Hour Reduction D _{Tc} (o/a) |
|---|--|---|
| Ferrous Sulfamate | 0.89 | 0.80 |
| Butylaldehyde | 0.92 | 0.82 |
| Iso-Butylaldehyde | 0.88 | 0.84 |
| Acetohydroxamic acid (AHA) | 0.82 | 0.88 |
| Hydroxylamine nitrate | 0.89 | 0.84 |
| Ave ± Std | 0.88 ± 0.04 | 0.84 ± 0.03 |
| Control (no reductant) | 0.90 | |
| N ₂ H ₄ (0.02 M) check ^a | 0.007 | |

a) No precipitate of Tc or TcO₂ was observed.

Table 3. Effect of Acetohydroxamic Acid (AHA) on the TBP (30% in Dodecane) Extraction (O/A = 1) of TcO_4^- ($1-1.5 \times 10^{-4}$ M) from HNO_3 Solutions.

| Reductant | [HNO_3] | | | |
|--|--------------------|------|------|-------|
| | 0.1 | 1.0 | 3.0 | 6.0 |
| No AHA immediate | 0.36 | 0.83 | 0.25 | 0.022 |
| AHA (0.01 M) immediate | 0.36 | 0.83 | 0.22 | 0.027 |
| AHA (0.01 M) 1 hour | 0.32 | 0.84 | 0.24 | 0.026 |
| N_2H_4 check (1M) (immediate, 25°C) ^a | 0.027 | | | |
| AHA (0.01 M) 1 hour (60°C) | 0.26 | 1.01 | 0.28 | 0.039 |
| Pruett (60°C) ^b | 0.30 | 0.80 | 0.20 | 0.030 |

a) No precipitate of Tc or TcO_2 was observed.

b) D. J. Pruett, reference 9.

Table 4. Effect of Acetohydroxamic Acid (AHA)^a on the TBP (30% in Dodecane) Extraction (O/A = 1) of TcO_4^- (1×10^{-4} M, + ^{95m}Tc tracer) from $\text{UO}_2(\text{NO}_3)_2$ Solutions at 1 M HNO_3 .

| Reductant 1 hour reduction | [$\text{UO}_2(\text{NO}_3)_2$] | | |
|--|----------------------------------|-------|------|
| | 0.77 | 1.0 | 1.23 |
| No AHA (25°C) | 0.59 | 0.47 | 0.41 |
| AHA (0.01 M) (25°C) ^a | 0.54 | 0.43 | 0.32 |
| Pruett ^b | 0.50 | 0.41 | |
| No AHA (40°C) | | 0.45 | |
| AHA (0.01 M) (40°C) ^a | | 0.46 | |
| Pruett ^b | | 0.41 | |
| No AHA (60°C) | | 0.48 | |
| AHA (0.01 M) (60°C) ^a | | 0.46 | |
| Pruett ^b | 0.50 | 0.41 | |
| No AHA (90°C) | | 0.47 | |
| AHA (0.01 M) (90°C) ^a | | 0.49 | |
| N_2H_4 (0.02 M) check ^c | | 0.007 | |

a) AHA causes the solution color to turn from yellow to gold, color returns to yellow by the end of reduction time.

b) D. J. Pruett, reference 9.

c) No precipitate of Tc or TcO_2 was observed.

concentrations at 60°C are shown in the table for comparison. Again no reduction is observed even after a one-hour reduction time. The maxima in the D_{Tc} vs. $[\text{HNO}_3]$ data, at both temperatures, are consistent with Pruett's data which also show maxima at ~1 M HNO_3 . A UV-VIS study of the reaction of pertechnetate with AHA in 2 M NaOH, at 25°C, also showed no reaction over 2 hours. The reduction of TcO_4^- (2×10^{-5} M) by 0.001

M N_2H_4 in 2 M NaOH was also followed by UV-VIS. The reduction is complete in 30 minutes following a 10-15 minute induction period.

Adding uranyl nitrate to the nitric acid matrix does not cause pertechnetate to reduce either (Table 4). The AHA in the aqueous phase was allowed to react for one hour (at 25°C, 40°C, 60°C or 90°C) before contacting it with TBP for one hour at room temperature. The non-AHA samples also went through this treatment. The technetium distribution coefficients for the AHA systems, when compared to non-AHA systems, were not significantly different. The distribution coefficients were also consistent with Pruett's data for $\text{UO}_2^{2+}/\text{TcO}_4^-/\text{HNO}_3$ systems.⁹ The extraction of technetium in the presence of hydrazine was used as a check sample for these experiments. Its distribution coefficient was two orders of magnitude lower than either the AHA or non-AHA systems indicating a definite reduction. No reduction of pertechnetate was observed for the counter experiment: constant uranyl concentration with variable acid concentration (Table 5). Likewise, no reduction was observed when the AHA concentration was varied in a 1 M $\text{UO}_2^{2+}/1$ M HNO_3 system (Table 6).

The uranium distribution coefficients in Table 6 and 7 were also consistent with Pruett's data indicating that AHA had no effect on its extraction. However, it was noted that AHA turns the color of the aqueous uranium solution from yellow to a golden or reddish-brown color. The intensity and shade of the color is directly dependent on the uranium and AHA concentrations but is inversely dependent on the acid concentration. The color diminishes with time and the fading occurs faster at higher temperatures; this effect could be due to the hydrolysis of the AHA.⁶ The organic phase containing

Table 5. Effect of Acetohydroxamic Acid (AHA)^a on the TBP (30% in Dodecane) Extraction (O/A = 1) of TcO_4^- (1×10^{-4} M, + $^{95\text{m}}\text{Tc}$ tracer) from 0.77 M $\text{UO}_2(\text{NO}_3)_2$ Solutions at Various HNO_3 Concentrations.

| Reductant | [HNO_3] | | | |
|-------------------------|--------------------|------|------|------|
| 1 hour reduction (25°C) | 0.62 | 0.77 | 1.0 | 1.76 |
| No AHA | 0.65 | 0.62 | 0.57 | 0.40 |
| AHA (0.01 M) | 0.69 | 0.48 | 0.54 | 0.38 |
| Pruett ^b | 0.62 | 0.53 | 0.50 | 0.40 |

a) Golden color of AHA solution is inversely acid dependent; lower acid more intense color.

b) D. J. Pruett, reference 9.

Table 6. Effect of Acetohydroxamic Acid (AHA)^a on the TBP (30% in Dodecane) Extraction (O/A = 1) of TcO_4^- (1×10^{-4} M, + $^{95\text{m}}\text{Tc}$ tracer) and Uranium from 1.0 M $\text{UO}_2(\text{NO}_3)_2/1$ M HNO_3 Solution at Various AHA Concentrations.

| 1 hour reduction (25°C) | [AHA] 0.01 | | [AHA] 0.05 | | [AHA] 0.10 | |
|-------------------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|
| | D_{Tc} | D_{U} | D_{Tc} | D_{U} | D_{Tc} | D_{U} |
| AHA | 0.44 | 0.85 | 0.41 | 0.80 | 0.39 | 0.78 |
| Pruett ^b | 0.40 | 0.80 | 0.40 | 0.80 | 0.40 | 0.80 |

a) The golden color becomes more intense as [AHA] increases.

b) D. J. Pruett, reference 9.

Table 7. Effect of Acetohydroxamic Acid (AHA)^a on the TBP (30% in Dodecane) Extraction (O/A = 1) of Uranium from 1.0 M $\text{UO}_2(\text{NO}_3)_2$ /1 M HNO_3 Solution at Various Temperatures.

| 1 hour reduction | [°C] | | |
|---------------------|------|------|------|
| | 40 | 60 | 90 |
| No AHA | 0.95 | 1.05 | 0.86 |
| AHA | 0.91 | 0.79 | 0.99 |
| Pruett ^b | 0.83 | 0.72 | |

a) The golden color fades during the reduction time.

b) D. J. Pruett, "reference 9.

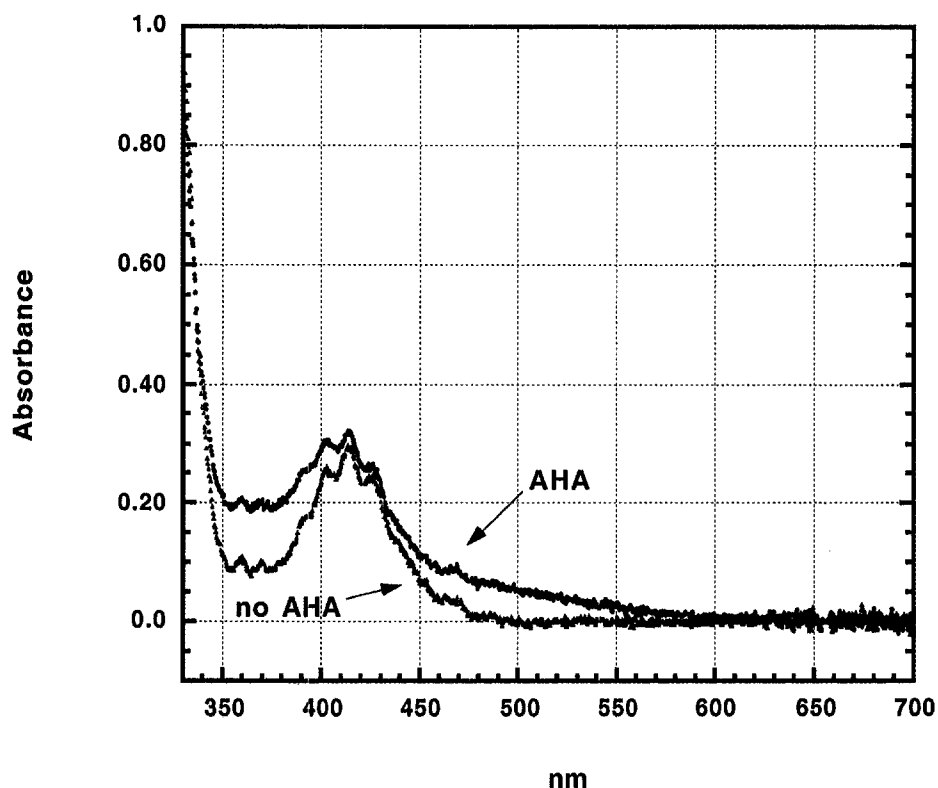


Figure 3. UV-Vis Spectrum of 0.05 M $\text{UO}_2(\text{NO}_3)_2$ in 0.05 M HNO_3 With and Without AHA present.

extracted UO_2^{2+} always had a yellow color that was not dependent on the nitric acid or AHA concentration. Although there was a noticeable color change of the uranium solutions when AHA was added to them there does not seem to be a significant change in the UV-VIS spectrum of uranyl nitrate solution. (Figure 3).

A tentative flowsheet (Figure 1) has been proposed for a countercurrent demonstration of the UREX process. An initial test of the flowsheet was performed with some minor changes. The first was that the feed UO_2^{2+} concentration was 1 M instead of 1.2 M. The second was that the AHA was added to the aqueous phase and then the aqueous phase was immediately contacted with TBP for two minutes (O/A = 3/1). It took another five minutes to centrifuge and separate phases. The color of the aqueous phase was golden to reddish-brown after the contact which suggests that UO_2^{2+} was affected by the AHA (i.e., complexed or reduced and complexed). The reason for rushing the experiment was to maximize any effect AHA would have on the system. The technetium and uranium distribution coefficients and the technetium fraction extracted are given in Table 8.

The TBP phase from the extraction was scrubbed with 0.5 M HNO_3 /0.3 M AHA at an O/A ratio of 4.64 instead of 5. This contact was also very short (two minutes) followed by a fast separation (five minutes). The aqueous phase had a golden brown color. The TBP phase from the scrub was stripped with 5.5 M HNO_3 at an O/A ratio of 7.4 instead of 1.0. The aqueous phase was almost colorless indicating that most of the uranium was in the TBP phase. The technetium and uranium distribution coefficients and the technetium fraction extracted²¹ are given in Table 8. If 66% of the technetium is extracted per stage then > 95% of the technetium should be extracted within 5 stages. The strip phase ratio was a mistake and is reflected in the high percentage of technetium that remains in the organic phase, 66%.

A second test of the proposed flowsheet (Table 9) was performed using the phase ratios shown in Figure 1. The AHA reduction was allowed to proceed for 1 hour before the TBP extraction was performed. The D_{Tc} for the extraction contact was similar to the fast experiment. The D_{Tc} for the scrub contact was lower in this experiment compared to the first experiment. There is no obvious explanation for this effect. The initial strip D_{Tc} was lower than in the first experiment (which is good) and reflects the use of a better phase ratio for this contact. The second strip D_{Tc} was higher than the first strip D_{Tc} which may indicate that some species other than pertechnetate was present in the TBP phase. A fourth strip containing N_2H_4 was performed to scavenge the remaining pertechnetate from the TBP. The hydrazine should have produced TcO^{2+} which is not extracted by TBP unless it becomes complexed by a soluble organic ligand.²² Surprisingly, the D_{Tc} was 2.68 which may indicate that a reduced Tc(IV) or (V) complex with AHA may have been formed and this species is soluble in the TBP phase. A pink technetium complex is formed when an acidic pertechnetate/AHA solution is reduced with hydrazine and then

Table 8: Rapid Test of the Proposed UREX Flowsheet Shown in Figure 1.^a

| | <u>Distribution Coefficients</u> | | <u>Technetium Fraction Extracted</u> |
|-------------------------------------|----------------------------------|----------------|--|
| | D_{Tc} | D_{U} | |
| Extraction (O/A = 3/1) | 0.66 | 2.34 | 0.66 |
| Scrub 1 (O/A = 4.64/1) ^b | 0.84 | 2.44 | 0.80 |
| Strip (O/A = 7.4/1) ^c | 0.24 | ---- | 0.64 |

^a AHA was added to the aqueous phase and then the aqueous phase was immediately contacted with TBP for 2 minutes and 5 minutes to centrifuge and separate phases.

^b 2 minute contact and 5 minutes to centrifuge and separate phases. Aqueous phase was a golden brown color.

^c The aqueous phase was almost colorless.

Table 9: Test of the Proposed UREX Flowsheet Shown in Figure 1.^a

| | Distribution Coefficients | | Technetium Fraction Extracted |
|--|----------------------------------|----------------------|--------------------------------------|
| | D_{Tc} | D_U | |
| Extraction (O/A = 3/1) ^a | 0.61 | 1.85 | 0.64 |
| Scrub 1 (O/A = 5/1) ^b | 0.66 | 1.96 | 0.77 |
| Strip 1 (O/A = 1/1) ^c | 0.16 | 62 | 0.14 |
| Strip 2 (O/A = 1/1) | 0.30 | ---- | 0.23 |
| Strip 3 (O/A = 1/1) | ---- | ---- | ---- |
| Strip 4 (O/A = 1/1, N ₂ H ₄) ^d | 2.68 | ---- | 0.74 |
| U Re-Ext 1 (O/A = 1/7) | 0.069 | ---- | 0.01 |

^a 1 hour AHA reduction of aqueous phase, 1 hour contact. Aqueous phase was a golden brown color.

^b 1 hour contact. Aqueous phase was a golden brown color.

^c 1 hour contact. Aqueous phase was light yellow color.

^d N₂H₄ should have reduced pertechnetate and helped the stripping.

neutralized with base. It is not known at this point whether this complex exists under acidic conditions.

The D_U values were significantly different between the two flowsheet experiments. More uranium extracted in the rapid experiment test. This is consistent with the color change that occurs when AHA is added to uranium solutions and the fading of the color with time. Thus it would appear that a UO²⁺/(AHA) complex is formed which is extractable into TBP. The D_U for the strip, 62, is an excellent value and indicates that most of the uranium will stay in the TBP phase during the technetium stripping step. This value does seem high. However, the estimated concentration of uranium in the organic phase going into the scrub contact was calculated to be 0.15 M. Based on this concentration the D_U is actually quite similar to other data.²³

Technetium needs to be recovered from the strip solutions and converted to a technetium target. The basic plan for recovery is to:

1. Add N₂H₄ and then neutralize the 5.5 M nitric acid solution with NaOH to produce TcO₂.
2. Oxidize the recovered TcO₂ with H₂O₂ to produce a concentrated solution of HTcO₄.
3. Neutralize with NH₄OH to form NH₄TcO₄, concentrate and crystallize.

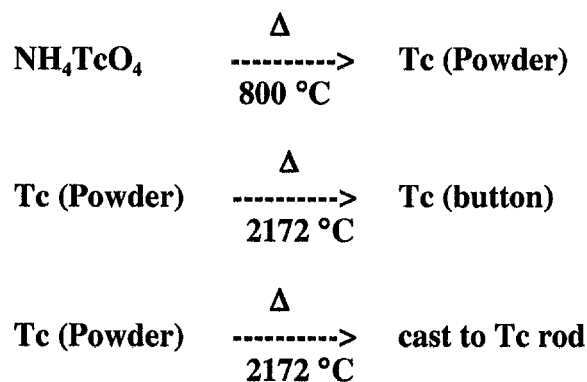
Alternatives to step one above are needed to minimize the generation of waste NaNO₃. Chemical denitration with sugar or formaldehyde are non-residual solutions to this problem.²⁴ Evaporation of the nitric acid would allow the acid to be recycled. However, strong heating of the solution may volatilize technetium as Tc₂O₇ (bp = 316°C). In our experience this has not been a significant problem. The second strip solution in Table 9 was concentrated 60 times by evaporation on a hot plate. One hundred percent of the technetium was retained. Likewise, the first strip solution was taken to dryness with 98% retention.

The third strip solution which had the lowest technetium concentration did not produce TcO₂ when the three step procedure above was tried without the nitric acid evaporation step. Formation of TcO₂ was possibly hindered by contaminants in the strip solution. Possible contaminants are TBP and its breakdown products (dibutylphosphate),

dodecane, uranium, and AHA and its hydrolysis products (hydroxylamine and acetic acid). Tests were performed to determine what contaminants prevented the precipitation of TcO_2 . Model systems consisting of TcO_4^- in 1 M or 5.5 M HNO_3 work fine. A 1 M HNO_3 /1 M UO_2^{2+} model system co-precipitates uranium and technetium oxides. More washes of the aqueous phase with fresh TBP solution may remove residual uranium. A 1 M or 5.5 M HNO_3 solution with dibutylphosphate allows some precipitation of the oxide. A 5.5 M HNO_3 solution saturated with TBP allows some precipitation of the oxide. More washes of the aqueous phase with fresh dodecane may remove residual TBP. A 1 M HNO_3 /0.1 M AHA model system forms a pink complex that prevents precipitation of TcO_2 . Evaporation of the nitric acid should hydrolyze the AHA and prevent this interference. Thus it appears that all the potential contaminants may interfere with the TcO_2 recovery. For this reason and to minimize the amount of NaNO_3 waste generated we chose to evaporate the sample before trying to precipitate TcO_2 .

The dried residue from strip one was carried through two TcO_2 precipitations and recovered 88% of the technetium. After dissolution with peroxide the solution had a yellow color. A liquid scintillation count of the sample shows that it was contaminated by uranium. A third precipitation of TcO_2 from the second precipitation supernate was unsuccessful probably because of the low technetium concentration relative to residual contaminants. Although the strips went through the uranium re-extraction step (Table 9) there is still enough uranium and other contaminants to hinder the TcO_2 precipitation.

Once TcO_2 is converted to NH_4TcO_4 the scheme to convert it to Tc metal is shown below:



Under an inert atmosphere the ammonium ion acts as a reductant for pertechnetate. The last two steps, which require a temperature of 2172 °C, can be achieved with an arc melter.

Lastly, technetium and uranium extraction coefficients were measured from an LWR simulant with and without AHA present (Table 10). The composition of the simulant is shown in Table 11.²⁵ Some components listed in the table were not added because they would present waste disposal problems after the conclusion of the experiment. Lanthanum oxide was used for all the rare earth elements listed. There were no significant differences in the technetium and uranium distribution coefficients between the AHA and non-AHA samples. In addition there was not a significant difference between the LWR simulant numbers and the simpler 1 M UO_2^{2+} /1 M HNO_3 system. The

Table 10. Technetium and Uranium Extraction from LWR Simulant.^a

| Extraction (O/A = 1/1) | D Value | 1 M UO ₂ ²⁺ /1 M HNO ₃ |
|-----------------------------|---------|---|
| D _{Tc} | 0.42 | 0.47 |
| D _{Tc} (AHA 0.1 M) | 0.42 | 0.39 |
| D _U | 0.69 | 0.80 |
| D _U (AHA 0.1 M) | 0.79 | 0.78 |

^a 1 hour reduction time followed by a 1 hour contact

Table 11: LWR Simulant ^{a,b,c}

| Element | Concentration (mol/L) | Element | Concentration (mol/L) |
|------------------------|-----------------------|-----------------------|-----------------------|
| μ | 4.7 | Sb | 0.000047 |
| HNO₃ | 1^d | Ce | 0.0077 |
| Nitrate | 3.3 | La | 0.043 |
| U | 1 | Ba | 0.0055 |
| Na | 0.0028 | Pd | 0.0063 |
| Sr | 0.0036 | Pr | 0.0042 |
| Ni | 0.002 | Al ^e | 0.0011 |
| Cr | 0.003 | Cs | 0.0087 |
| Fe | 0.0011 | Eu | 0.00066 |
| Mn | 0.00033 | K^e | 0.00097 |
| Te | 0.0025 | Mg ^e | 0.0016 |
| Se | 0.0003 | Gd | 0.00047 |
| Zr | 0.00013 | Sm | 0.0027 |
| Mo | 0.018 | Ca^e | 0.00095 |
| Pb | 0.0016 | Cd | 0.00043 |
| Ru | 0.01 | Sn | 0.00022 |
| Y | 0.0022 | Rh | 0.0016 |
| Nd | 0.013 | Ag | 0.00028 |

^a N. Boukis and E. Henrich, reference 25.

^b Elements not in bold face were not used for ES&H or other reasons.

^c La(NO₃)₃ was used for all the lanthanides.

^d pH measurements of the simulant indicate an [H⁺] of 0.9 M.

^e elements left out of the second LWR simulant.

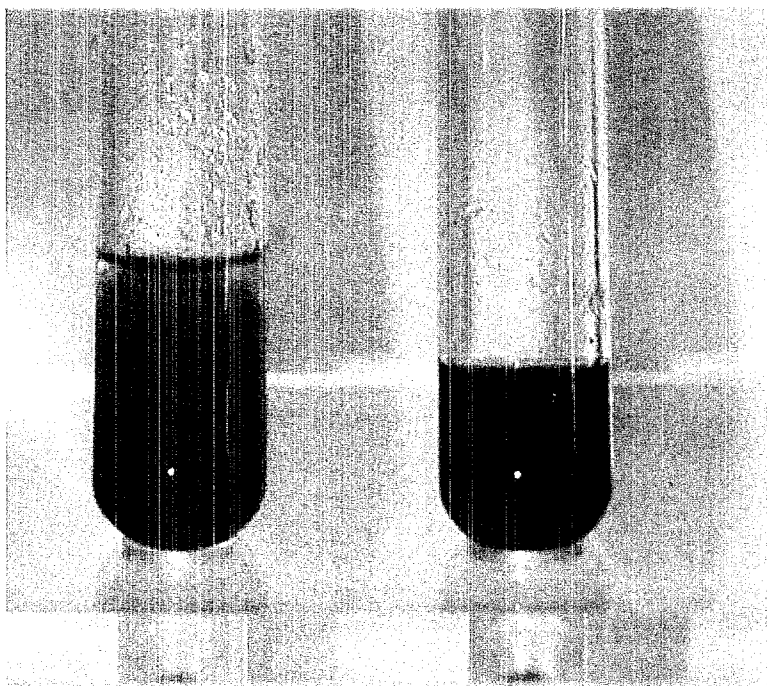


Figure 4. Gelatinous LWR/AHA Simulant with TBP (left). Precipitate in LWR/AHA Simulant (right).

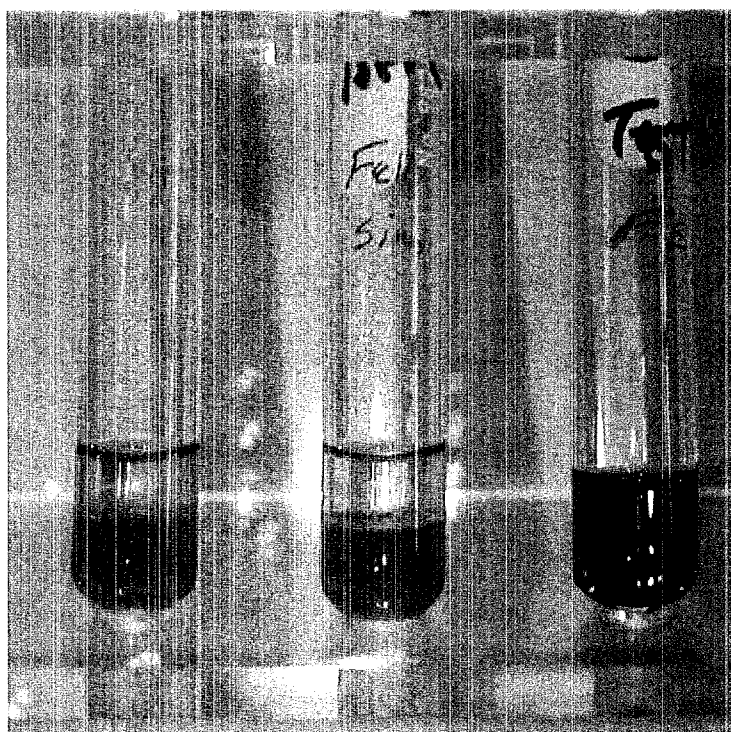


Figure 5. After 48 hours. LWR Simulant with TBP (left). LWR/AHA Simulant with TBP (middle). LWR/AHA Simulant (right).

data in Table 10 do not tell the whole story. Ten minutes after adding AHA to the LWR simulant the solution became cloudy and after one hour a yellow-brown precipitate had formed (Figure 4). Since this precipitation does not occur in the 1 M UO_2^{2+} /1 M HNO_3 system the precipitate would not appear to be due to uranium. AHA type ligands forms complexes with many metals including Cr, Fe, Ni, Mo, Ru, Rh, Pd U, the rare earths, and Al.²⁶ Thus there are many candidates in the LWR simulant that may be causing the precipitation. Without filtering, the AHA sample was contacted with TBP for one hour. The sample appeared gelatinous after the contact. Centrifuging resulted in a precipitate and an interfacial scum between the aqueous and TBP phases. In addition, a scum was on the walls of the tube as high as the organic phase. Addition of AHA and immediately contacting with TBP forms a gel (Figure 4). Except for a small interfacial scum, the non-AHA samples were relatively free of any of these problems. After 48 hours the AHA sample clears up, no precipitate, gel or scum was present.

A new simulant was prepared that was the same as that in Table 11 except that Al, K, Ca and Mg were left out of the formulation since they are not normally present in dissolved LWR fuel. This simulant gave essentially the same behavior as the first LWR simulant. Pretreating the TBP solution with a 0.5 M Na_2CO_3 scrub and two water washes marginally improved the behavior of the LWR simulant.

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Part 2. Iodine Removal from UREX Feed Solutions

The ATW program requires that greater than 95% of the iodine in spent LWR fuel be removed and trapped during the dissolution of the fuel and/or prior to running the dissolved fuel (feed) through the UREX process. This work focuses on the iodine removal from the feed solution before it enters the UREX process. It is vital to establish the major parameters that affect the removal of I_2 from the feed solution.

Boukis and Henrich have described a two-step procedure for removing iodine from dissolved nuclear fuel solutions using a sparging gas system of N_2/O_2 and NO_x .¹ The latter gas was used to reduce iodates back to iodine. Their goal was to remove 98 to 99% of the iodine. They accomplished this goal by going through a complex method of adding additional non-radioactive carrier iodide and iodate (an oxidant for organoiodides) and continuing the sparging. Since the ATW removal goal is not as high as that described by Boukis and Henrich a simple sparging with N_2 may be adequate. Because of the need to limit the amount of iodine that will be recovered and transmuted the addition of extra iodine to the system is undesirable.

An experimental design approach was used to determine the major factors that would volatilize iodine from a simple feed simulant solution. Six factors studied were:

1. the concentration of HNO_3 in the feed solution to mimic the nitric acid used in spent fuel processing,
2. the concentration of $NaNO_3$ to represent the ionic strength that uranyl nitrate would give to the feed solution,
3. the flow rate of nitrogen gas (N_2) that transports the volatile iodine to the sodium hydroxide traps,
4. the temperature of the feed solution,
5. the concentration of iodine in the feed solution, and
6. the total time that the nitrogen gas sparges the system.

A full factorial design for n factors requires 2^n experiments; thus 64 experiments would be needed to define the present system. Because we were interested in determining the best way to remove iodine from more complex solutions, a scoping study using a two level design in a fractional factorial mode was used to determine the main factors that would influence I_2 volatilization from a feed solution. This approach only required 8 experiments to screen the factors. The design using the maximum and minimum values for the experimental parameters is given in Table 1. The value Y is the percentage of iodine removed from the feed solution or sequestered in the trap.

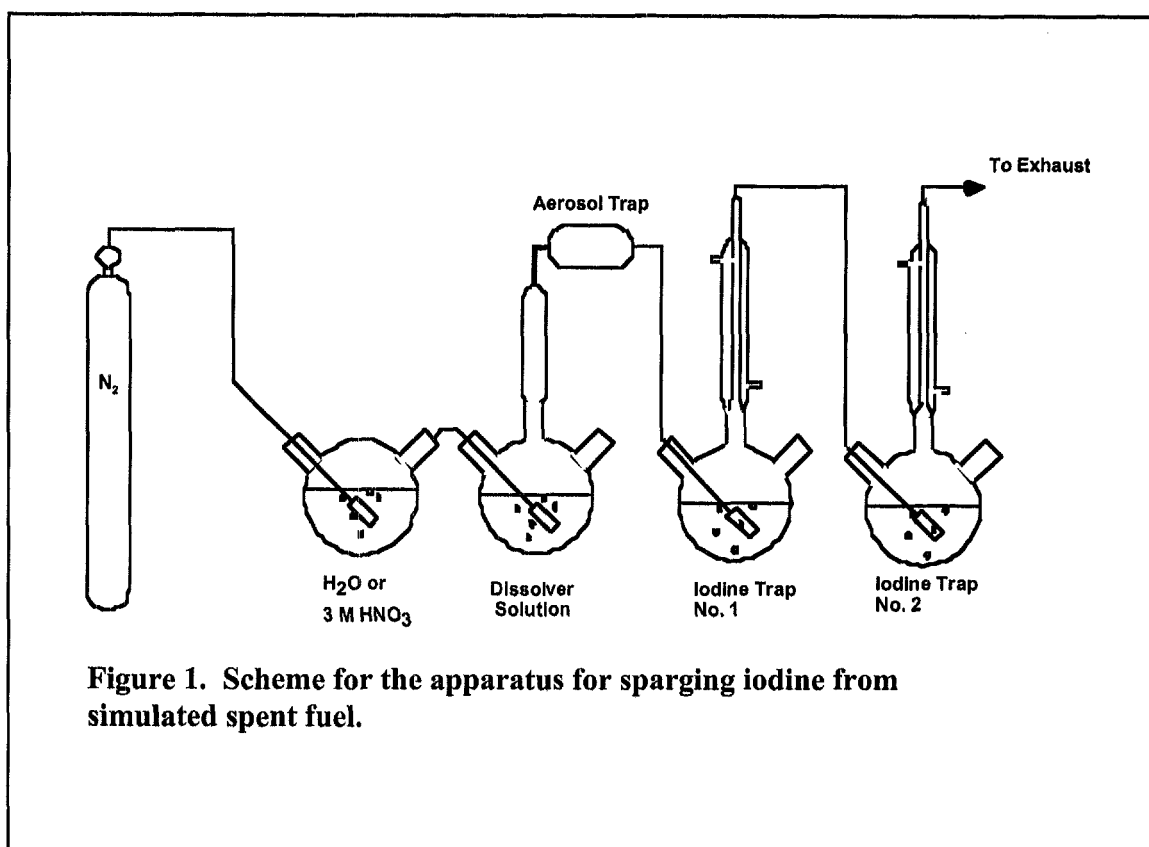
Following the completion of the experimental design, a screening model was executed to find the combination of factors that optimized the volatilization and transport of iodine from the feed solution. The screening model investigated the removal of iodine from two different perspectives. First, the removal of the iodine from the feed solution without concern for the amount of iodine collected in traps 1 or 2. Second, the sequestering of the iodine in trap 1 without regard to the total iodine removed from the reaction pot. Using the screening model profile tools, a comparison between the two perspectives was possible. Based on the results of the analysis, the optimum condition for removing iodine from a uranium/nitric acid system were proposed and tried.

Table 1. Two-level, Fractional Factorial Experimental Design for Optimizing the Factors that Effect the I₂ Volatilization from a Feed Solution.

| Experi ment # | Design Pattern (+) = max. (-) = min. | HNO ₃ (M) | N ₂ Flow Rate (mL/min) | NaNO ₃ Ionic Strength (M) | Feed Solution Temp. (°C) | Iodide (M) | Time (min) | Y |
|---------------------|---|-------------------------|---|---|-----------------------------------|---------------|---------------|---|
| 1 | - + - + - | 1 | 200 | 3 | 25 | 0.001 | 30 | • |
| 2 | + - - - + | 5 | 50 | 3 | 25 | 1e-7 | 120 | • |
| 3 | + + + + + | 5 | 200 | 3 | 95 | 0.001 | 120 | • |
| 4 | - - + - + | 1 | 200 | 0 | 95 | 1e-7 | 120 | • |
| 5 | - - + + - | 1 | 50 | 3 | 95 | 1e-7 | 30 | • |
| 6 | + + - - - | 5 | 200 | 0 | 25 | 1e-7 | 30 | • |
| 7 | - - - - + | 1 | 50 | 0 | 25 | 0.001 | 120 | • |
| 8 | + - - + - | 5 | 50 | 0 | 95 | 0.001 | 30 | • |

Experimental: All reagents were analytical grade or better and were obtained from Aldrich or Fisher. All water used was 18 MΩ prepared by passing distilled water through a Millipore Milli-Q water system. Iodine-125 tracer was purchased from New England Nuclear. A NaI γ-counter, a Packard Auto-Gamma[®] 5000, was used to measure the 35.49 keV γ-emission from ¹²⁵I in the samples. Figure 1 is a schematic of the iodine sparging apparatus: 250 mL, 2 or 3 neck, 24/40 ST flasks were used with 20-cm condensers. Flexible Teflon tubing connected different parts of apparatus together. Figures 2 and 3 are photos of the apparatus that identify its parts and sections. Teflon sleeves were used to seal the ST joints. The condensers operated at ambient temperature. The vessel containing the iodine laden feed solution, had a thermal well, which allowed the temperature of the solution to be regulated (J-Kem Scientific Model 210). Nitrogen gas was regulated through the system with appropriate valves and flowmeters (Gilmont, 10", stainless steel ball). Coarse gas dispersion tubes were used to sparge the solutions. The gas was humidified and saturated with nitric acid by passing it through 16 M HNO₃ prior to sparging it into the feed solution. This was done to limit losses of nitric acid and water from the feed solution during a run. A quartz wool filter was placed on top of feed solution condenser to trap aerosols coming off the feed solution during high heat and/or high gas flow conditions. Iodine was trapped as iodide by reacting it with 1 M NaOH (100 mL) in the two trapping flasks. Sampling adapters, with Teflon stopcocks and septum ports, were fitted to the one of 24/40 joints on the feed solution flask and the first NaOH trap flask. These adapters allowed sampling of the solutions with a syringe fitted with a 12", 18 gauge, stainless steel, needle while gas-sparging experiments were being performed.

Four primary feed solutions of nitric acid and/or sodium nitrate were prepared: a) 1 M HNO₃, b) 1 M HNO₃ and 3 M NaNO₃, c) 5 M HNO₃, and d) 5 M HNO₃ and 3 M NaNO₃. The typical procedure was to add 100 mL of the appropriate feed solution to the feed flask and add 1-mL aliquots of either 0.1 M or 1 x 10⁻⁵ M sodium iodide solution and then spike the solution with 10-20 μL of ¹²⁵I tracer. After stirring and equilibrating for ten minutes a 1-mL aliquot of the feed solution was removed to determine the initial specific activity of ¹²⁵I in the feed solution. The solution was heated to the desired temperature and then N₂ gas was passed through the reaction vessel at the required flow rate. The start of gas flow was the starting time of the experiment. The solution in trap 1



was sampled for ^{125}I periodically. The temperature of the feed solution and the nitrogen gas flow were recorded periodically. The experimental design type experiments were stopped after flowing the N_2 gas through the system for a set amount of time. The feed solution and the NaOH solutions in trap 1 and trap 2 were sampled after the run was completed. All samples were weighed 1-mL aliquots. The sample aliquot was transferred to a tared 20-mL plastic vial containing 5 mL of water and counted. Counting data were decay corrected to a predetermined time.

The inventory of iodine between the feed vessel and the traps was determined by rinsing down the condensers and the connecting sections of the apparatus with DI water and counting the wash solution. This included the quartz wool aerosol filter (13) from section 14 that was also gamma counted. These rinses were useful for determining the iodine accountability in the system.

A test of the experimental design's ability to predict the removal and transport of iodine from a 1 M $\text{UO}_2(\text{NO}_3)_2/1$ M HNO_3 was performed by adding 91 mL of an aqueous solution containing 50.3 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the feed flask. After adding 1 mL of 0.1 M NaI and 0.1 mL of ^{125}I tracer the solution the temperature of the solution was raised close to 90°C . Then 6.25 mL of con HNO_3 was injected into the solution and the gas flow started at 200 mL/minute. The 35.49 keV γ -emission from the ^{125}I tracer is quenched by the dense uranium solution. The true activity of ^{125}I in these solutions was corrected using the equation:

$$\text{measured activity} = 1868 + (0.54065 \times \text{true } ^{125}\text{I activity}) \quad R = 0.99993$$

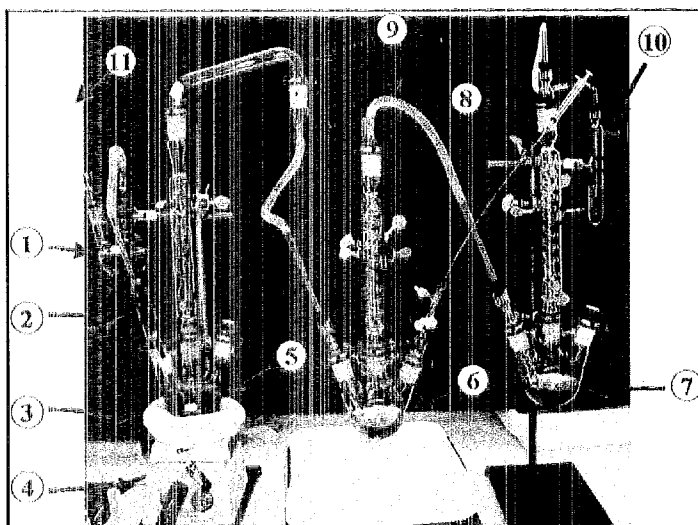


Figure 2. Photo of Apparatus and Identification of Sections: 1) 15.8 M HNO_3 , 2) thermocouple, 3) heating mantle for feed solution, 4) stir plates, 5) feed solution, 6) trap #1 (1 M NaOH), 7) trap #2 (1 M NaOH), 8) syringe/needle sampler, 9) condensers and connecting Teflon tubing, 10) exhaust to hood, 11) (not shown) flowmeters and nitrogen tank.

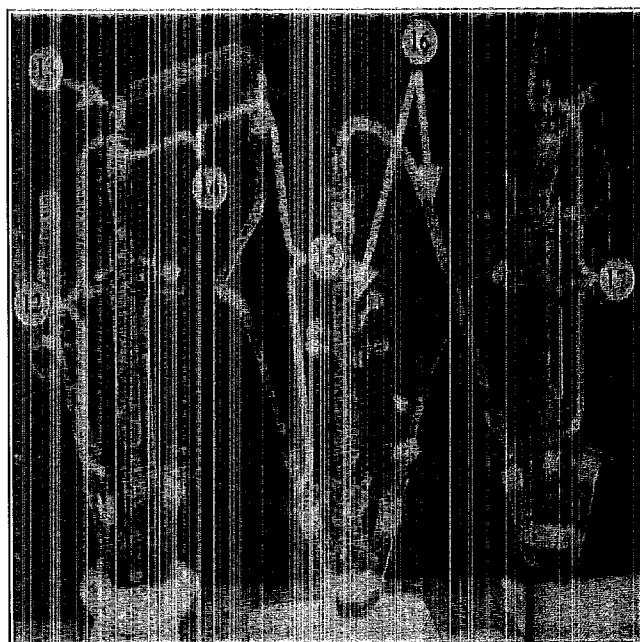


Figure 3. Identification of Connecting Sections of Apparatus: 12) feed solution condensing column, 13) quartz wool, 14) u-shaped connecting tube, 15) Teflon tubing leading to trap 1, 16) condensing column and Teflon tubing between traps 1 and 2, 17) condensing column leading from trap 2 to exhaust.

Results and Discussion: The percent of iodine removed from the feed solution for the eight experiments are given in Table 2 and 3. The results in Table 2 are based on the amount of ^{125}I remaining in the feed solution after the experiment was conducted. Runs 4 and 8 were, respectively, the low and high iodine removal experiments. The mean percent removal for this set of experiments was 36.5% ($R^2 = 0.963$). In contrast, Table 3 shows the results based on the percentage of iodine that was actually transported to trap 1. Runs 2 and 1 were, respectively, the low and high iodine transport experiments. The mean

Table 2. Removal of ^{125}I from the Feed Solution. Based on Feed Solution Inventory.

| Experi ment # | Design Pattern (+) = max. (-) = min. | HNO_3 (M) | N_2 Flow Rate (mL/min) | NaNO_3 Ionic Strength (M) | Feed Solution Temp. ($^{\circ}\text{C}$) | Iodide (M) | Time (min) | % Iodine Removed from the Feed Solution |
|---------------------|---|-----------------------|---------------------------------------|---|---|--------------------|---------------|---|
| 1 | -++-+- | 1 | 200 | 3 | 25 | 0.001 | 30 | 76.24 |
| 2 | +--+++ | 5 | 50 | 3 | 25 | 1×10^{-7} | 120 | 2.28 |
| 3 | ++++++ | 5 | 200 | 3 | 95 | 0.001 | 120 | 67.37 |
| 4 | -++-+- | 1 | 200 | 0 | 95 | 1×10^{-7} | 120 | 0.42 |
| 5 | --++-- | 1 | 50 | 3 | 95 | 1×10^{-7} | 30 | 7.24 |
| 6 | ++---- | 5 | 200 | 0 | 25 | 1×10^{-7} | 30 | 1.91 |
| 7 | ----++ | 1 | 50 | 0 | 25 | 0.001 | 120 | 41.78 |
| 8 | +--++- | 5 | 50 | 0 | 95 | 0.001 | 30 | 95.01 |

Table 3. Removal of ^{125}I from the Feed Solution. Based on the Trap 1 Inventory.

| Experi ment # | Design Pattern (+) = max. (-) = min. | HNO_3 (M) | N_2 Flow Rate (mL/min) | NaNO_3 Ionic Strength (M) | Feed Solution Temp. ($^{\circ}\text{C}$) | Iodide (M) | Time (min) | % Iodine Collected in Trap 1 |
|---------------------|---|-----------------------|---------------------------------------|---|---|---------------|---------------|------------------------------------|
| 1 | -++-+- | 1 | 200 | 3 | 25 | 0.001 | 30 | 69.41 |
| 2 | +--+++ | 5 | 50 | 3 | 25 | $1\text{e-}7$ | 120 | 0 |
| 3 | ++++++ | 5 | 200 | 3 | 95 | 0.001 | 120 | 67.4 |
| 4 | -++-+- | 1 | 200 | 0 | 95 | $1\text{e-}7$ | 120 | 5.95 |
| 5 | --++-- | 1 | 50 | 3 | 95 | $1\text{e-}7$ | 30 | 1.14 |
| 6 | ++---- | 5 | 200 | 0 | 25 | $1\text{e-}7$ | 30 | 0.97 |
| 7 | ----++ | 1 | 50 | 0 | 25 | 0.001 | 120 | 32.7 |
| 8 | +--++- | 5 | 50 | 0 | 95 | 0.001 | 30 | 55 |

percent transport for this set of experiments was 29.1% ($R^2 = 0.985$). Trap 2 never showed any activity throughout these experiments. The generally lower percentages for Table 3 are due to losses of iodine in the joints, glassware, delivery tubes to the traps, and significantly by the quartz wool plug used to prevent aspiration of feed solution to the trap 1 and Section 15 of the apparatus. Figure 4 shows the percent of the iodine reporting to trap 1 as a function of time, some of the 30 minute experiments were allowed to run longer than the allotted time but only the data to 30 minutes were used in the design.

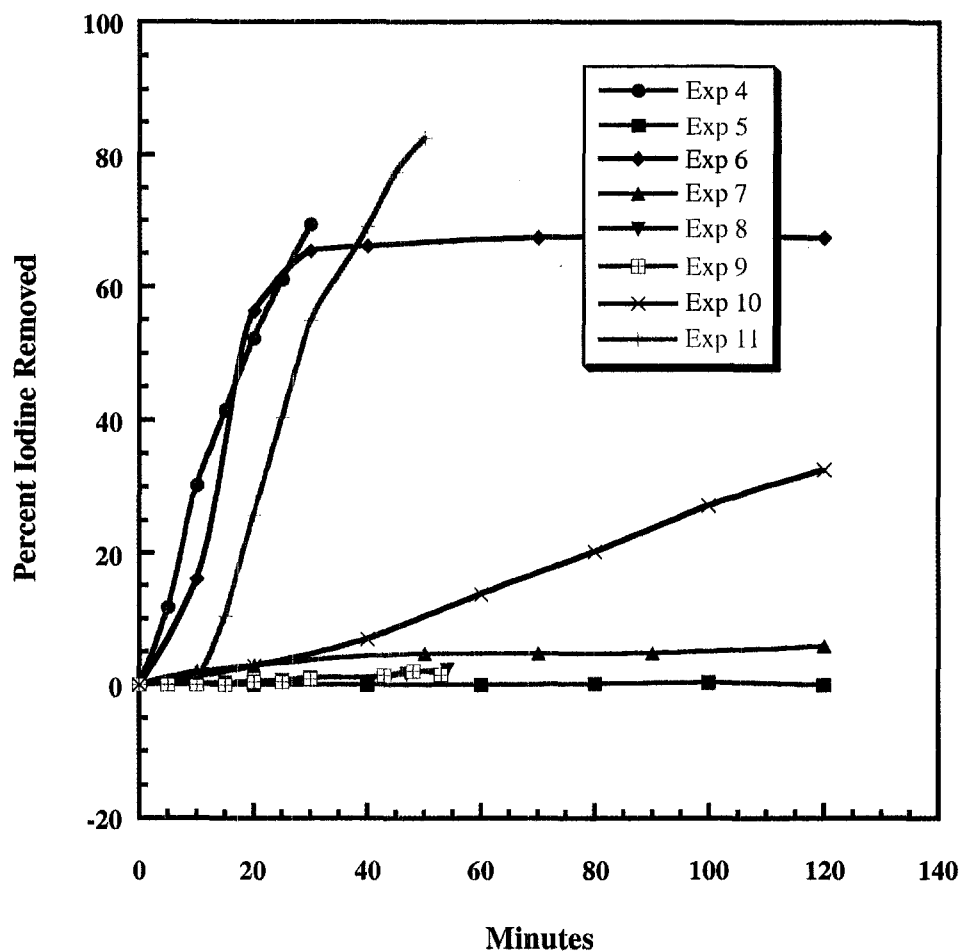


Figure 4. Percent Iodine Collected in Trap 1 as a Function of Time

Screening Fit

(Y)

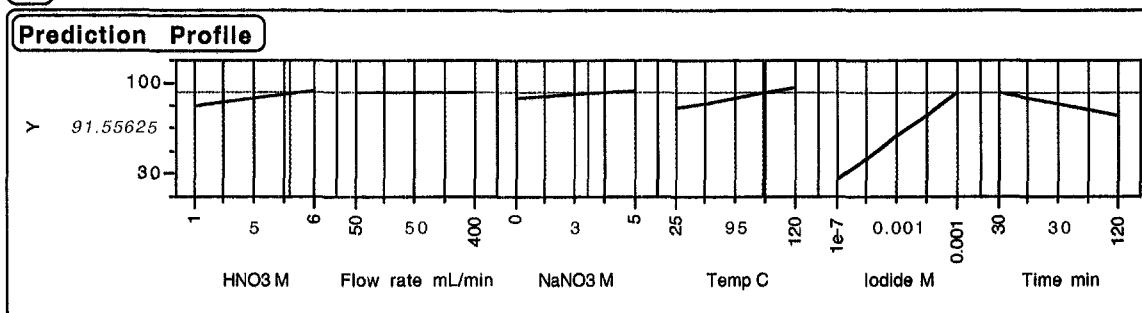


Figure 5. Optimized Factors for Removing Iodine from the Feed Solution. Factor values in red are the optimum values within the range of factor values studied that will effect 91.6% iodine removal from the feed solution.

Screening Fit

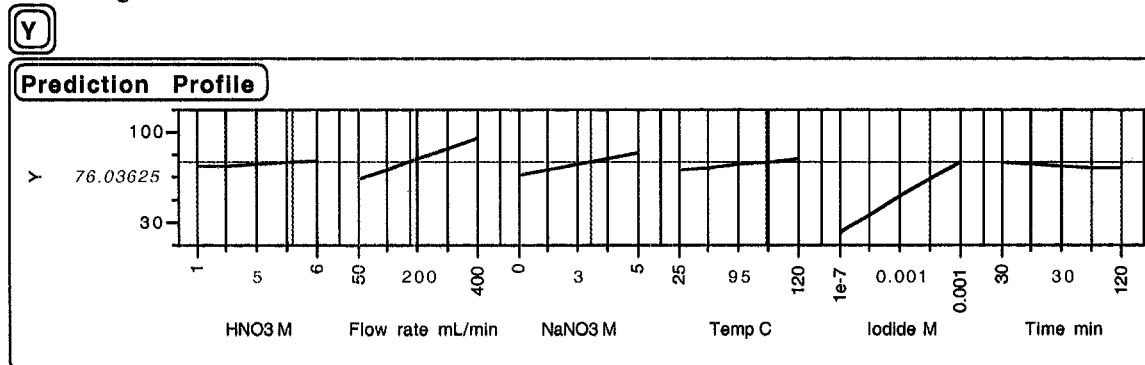
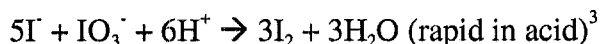


Figure 6. Optimized Factors for Transporting Iodine to Trap 1. Factor values in red are the optimum values within the range of factor values studied that will effect 76.0% iodine transport to trap 1.

The goal of the experimental design was to find the factors combinations that would either optimize the removal of iodine from the feed solution or the transport of iodide to the traps. The JMP program fitted a screening model to the data in Tables 2 and 3. The optimized factor levels (within the range of values used in the experimental design) from the perspective of the feed solution and trap 1 are shown in Figures 5 and 6, respectively. These figures have six profile plots for the six factors studied. The greater the influence of a factor on iodine removal or transport is reflected by a greater positive slope. The iodide concentration was a major factor from both points of view. This is reasonable based on the reaction stoichiometry and kinetics, iodide needs to be oxidized to I_2 the species that is volatilized and transported. At lower concentrations, the kinetics are slower because the combination of two iodine radicals is less probable. In addition, at low concentrations, a higher percentage of the iodide species in the solution may exist as non-volatile iodate. Since iodate reacts with iodide to by the reaction below lower concentration of iodide will slow this reaction down.



Other factors that were important for removing iodine from the feed solution are more easily illustrated by looking at the Bayes plot (Figure 7) for this point of view. The Bayes plot uses normalized factor estimates that have been transformed to be uncorrelated. This was required because the data was correlated. This plot again shows the huge effect the iodide concentration has on the system, accounting for >90% of the response. The order of factors that have a positive influence on the iodine removal from the feed solution are temperature > $[HNO_3]$ > $[NaNO_3]$. Because of the volatility of iodine it is not surprising that increasing temperatures will benefit the removal of iodine from the feed solution. Increasing the HNO_3 concentration increases the oxidation potential of the solution that promotes the oxidation of iodide to volatile iodine. The higher ionic strength caused by increasing the $NaNO_3$ concentration decreases the solubility of the neutral, non-polar, volatile I_2 molecule from the feed solution. The large negative effect of time may be an anomalous result since volatilization of iodine from the

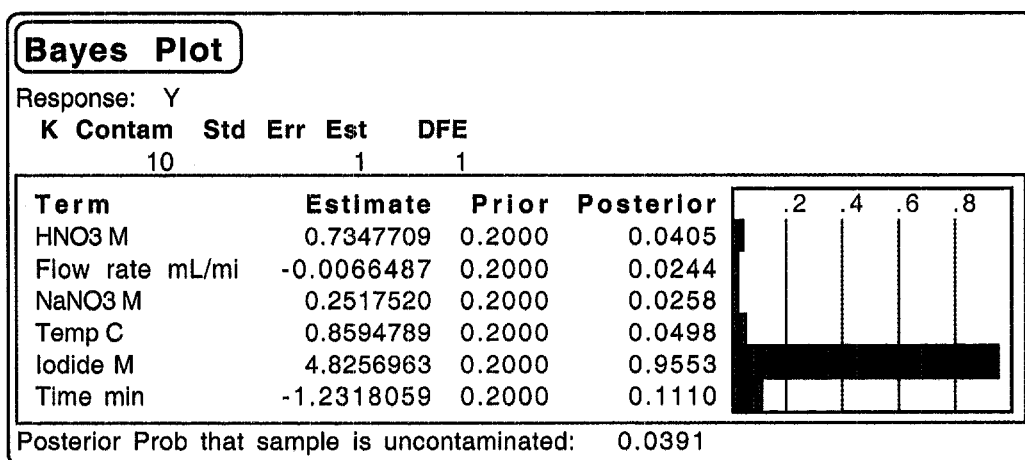


Figure 7. Bayes Plot for the Factors that Affect the Removal of Iodine from the Feed Solution.

Screening Fit

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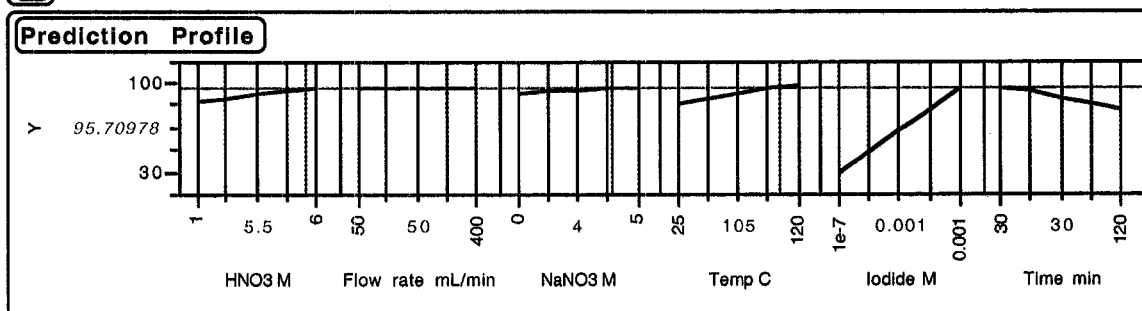


Figure 8. Optimized Factors for Removing >95% of the Iodine from the Feed Solution.

feed solution (likewise the transport to trap 1) will slow down with time no matter how the experiments are carried out. The model, being non-discriminatory, probably interprets time as a deleterious factor. Surprisingly, the gas flow rate has a small negative effect on iodine removal from the feed. However this factor's effect is so small it may be statistically no different than zero. Thus the natural volatility of iodine from the solution is unaffected by the gas flow rate.

In order to remove >95% of the iodine from the feed solution the conditions to enhance are the temperature, [HNO₃], and [NaNO₃]. This should be done while minimizing the nitrogen flow rate and the time. Although, the iodide concentration was a parameter used in the experiments it is not controlled in practical applications. That is, real feed solutions would contain variable amounts of iodine depending on the burn up of

the fuel and how much iodine was lost during fuel dissolution. Therefore, the concentration of iodide is not a factor that can be practically manipulated to improve iodine volatilization. However for the exercise discussed here the iodide concentration is maximized at 0.001 M. Figure 8 shows that >95% of the iodine should be removed by increasing the nitric acid concentration to 5.5 M, the sodium nitrate concentration to 4 M and the temperature to 105°C. This has a basis in reality because the sodium nitrate ionic strength is equivalent to a 1.3 M $\text{UO}_2(\text{NO}_3)_2$ solution, a concentration that is similar to proposed UREX feed solutions. The temperature required is near the boiling point of a 5.5 M HNO_3 /1.3 M $\text{UO}_2(\text{NO}_3)_2$ solution.¹

Figure 6 shows the optimized factors for transporting iodine to trap 1. The factor values are the optimum values within the range studied. At these levels they only move 76.0 % of the iodine to trap 1. Figure 9 shows the Bayes plot for the factors that affect the transport of iodine to the trap. The order of factors that have a positive influence on the transport of iodine to trap 1 are flow rate > $[\text{NaNO}_3]$ > temperature > $[\text{HNO}_3]$. Trap 1 relied heavily on higher flow rates of nitrogen gas to transport the volatile iodine through the apparatus to the trap. It is difficult to explain the relative importance of the sodium nitrate concentration over the temperature. Logically, volatilized I_2 would maintain its latent heat as it escapes from the feed solution. Higher temperatures should increase the vapor pressure I_2 and help it move through the apparatus to trap 1. Why should

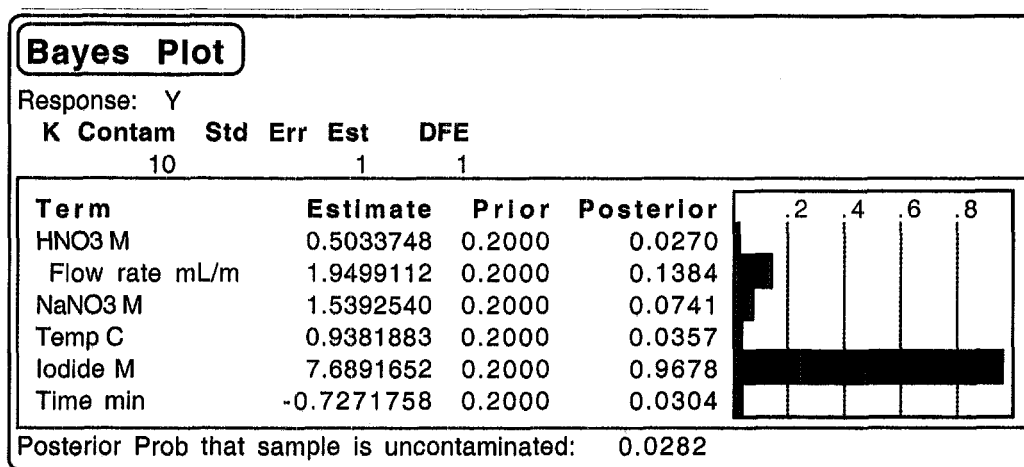


Figure 9. Bayes Plot for the Factors that Affect the Transport of Iodine to Trap 1.

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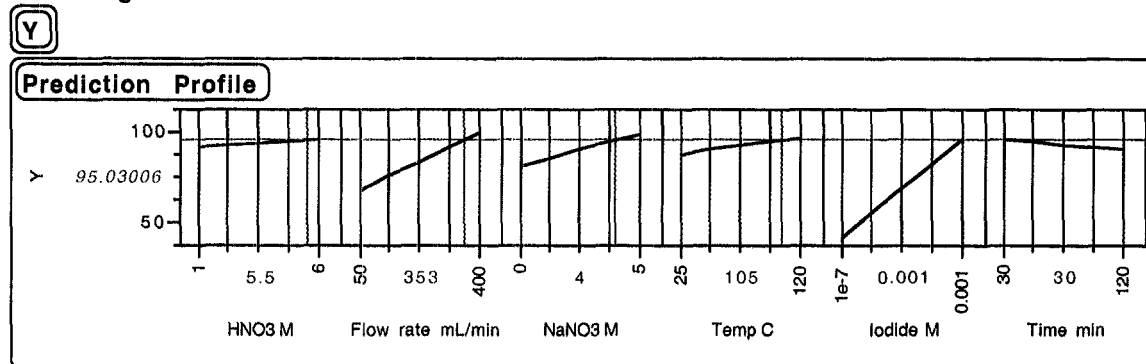


Figure 10. Optimized Factors to Transport >95% of the Iodine to Trap 1.

volatilized I_2 have any memory of $NaNO_3$? From the perspective of the trap, the concentration of nitric acid in the feed solution had little effect on the transport of I_2 .

In order to transport >95% of the iodine from the feed solution to trap 1, the conditions to enhance are the flow rate, temperature, $[HNO_3]$, and $[NaNO_3]$. The comments made previously about the iodide concentrations still apply, the iodide concentration is maximized at 0.001 M. Figure 10 shows that >95% of the iodine should be transported by increasing the nitric acid concentration to 5.5 M, the sodium nitrate concentration to 4 M, and the temperature to 105°C. Most importantly the flow rate is increased to 353 mL/min.

The bottom line for using the experimental design approach was to be able to predict the parameters that would achieve a certain result for the process being studied. Our combined goal was to remove 95% of the iodine from a UREX feed solution simulant, 1 M $UO_2(NO_3)_2$ /1M HNO_3 , and transport it to a trap. In this solution, the acid concentration and the non-acidic ionic strength (3M) contributed by the uranium nitrate, fixes two of the parameters. The important transport parameter, gas flow rate, was set to 200 mL /minute. Although higher flow rates are predicted to be better, the experiment needed to stay within the limits of the experimental apparatus and it was also desirable to keep all the parameters within the limits studied in the experimental design. Thus a temperature 90° C and a $[I^-]$ of 0.001M were used. For the reason explained above, a 30 minute run time was input into the feed solution and trap 1 models along with the other parameters. In practice the experiment was allowed to run for 113 minutes. Figures 11 and 12 respectively predict that 80% iodine will be removed from the feed solution and 72% of the iodine will be transported to trap 1 with these parameters. The experimental results are shown in Figure 13. Trap 1 collected 71% of the iodine in 30 minutes, a result in strong agreement with the prediction. Removal of iodine from the UREX simulant solution was much better than predicted, 93% removed within 30 minutes. However, no further iodine was removed from the UREX simulant solution even after 113 minutes. Thus the experiment fell slightly short of it goal of removing 95% of the iodine from the UREX solution. Since the residual iodine species appears to be non-volatile it is assumed that it is iodate. At 47 minutes, trap 1 had accumulated 93% and was no different after 113 minutes. The irregularity in the trap 1 curve at ~<10 minutes was probably due to

Screening Fit

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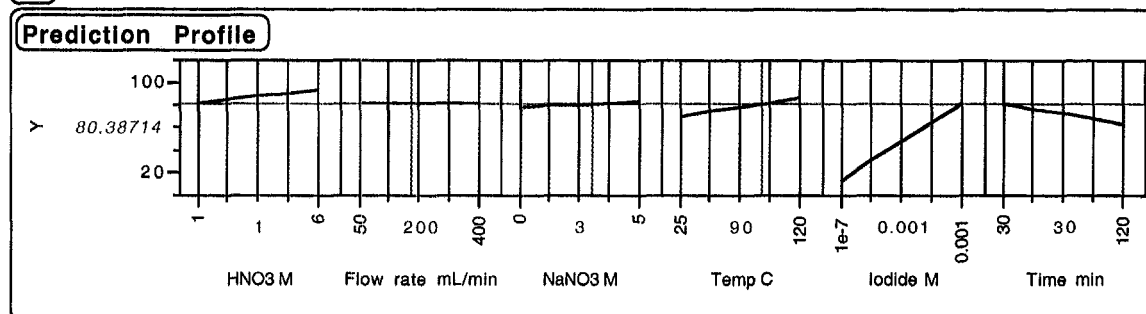


Figure 11. Prediction of Percentage of Iodine that would be Removed from a UREX Feed Solution Simulant (1 M $\text{UO}_2(\text{NO}_3)_2$ /1 M HNO_3) in 30 minutes.

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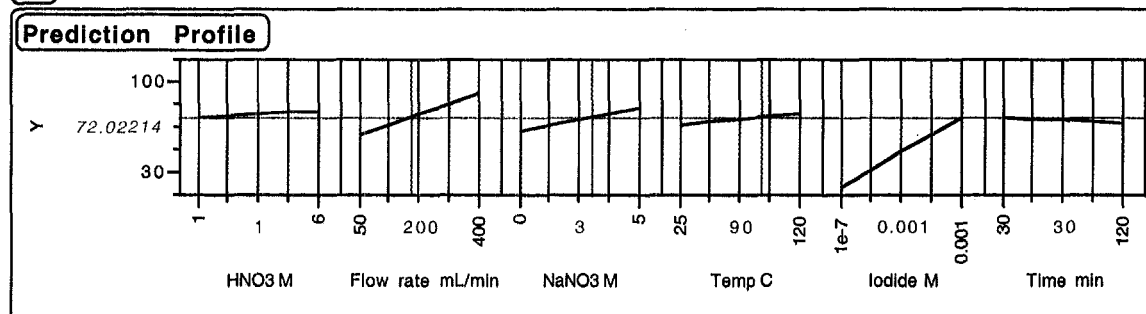


Figure 12. Prediction of the Percentage of Iodine that would be Transported to Trap 1 from a UREX Feed Solution Simulant (1 M $\text{UO}_2(\text{NO}_3)_2$ /1 M HNO_3) in 30 minutes.

iodine crystals that condensed in one of the side necks of the feed flask which slowed the transport to the trap.

Additional factors that could affect the removal of iodine from a real UREX solution are the formation of insoluble fission product iodides and iodates (i.e., AgI , RhI_3 , etc.).⁴ Organic contaminants are often found in nitric acid, on the fuel elements and machinery and piping used in plant operations.¹ Iodine radicals may react with these organics to form organoiodides, which may or may not be volatile. Thus a reservoir of non-volatile iodide species may build up in the system and threaten the processing goal of >95% iodine removal.

Consideration should be given to the trapping strategy that will be used to collect the iodine. The gases coming off will undoubtedly include nitrogen oxides, nitric acid, possibly some volatile fission products, iodine gas, and organoiodides. We have used as a matter of convenience a solution of sodium hydroxide. By its use NaI is produced. A possible improvement on this method of trapping iodide was suggested by Toth.⁵ Iodine passed through molten NaOH containing some Na reductant would form NaI as a primary phase that in principle could be easily separated on cooling the melt. Some

consideration should also be given to capture the iodine as solid I_2 . This will permit the purification of iodine by utilizing its sublimation properties.

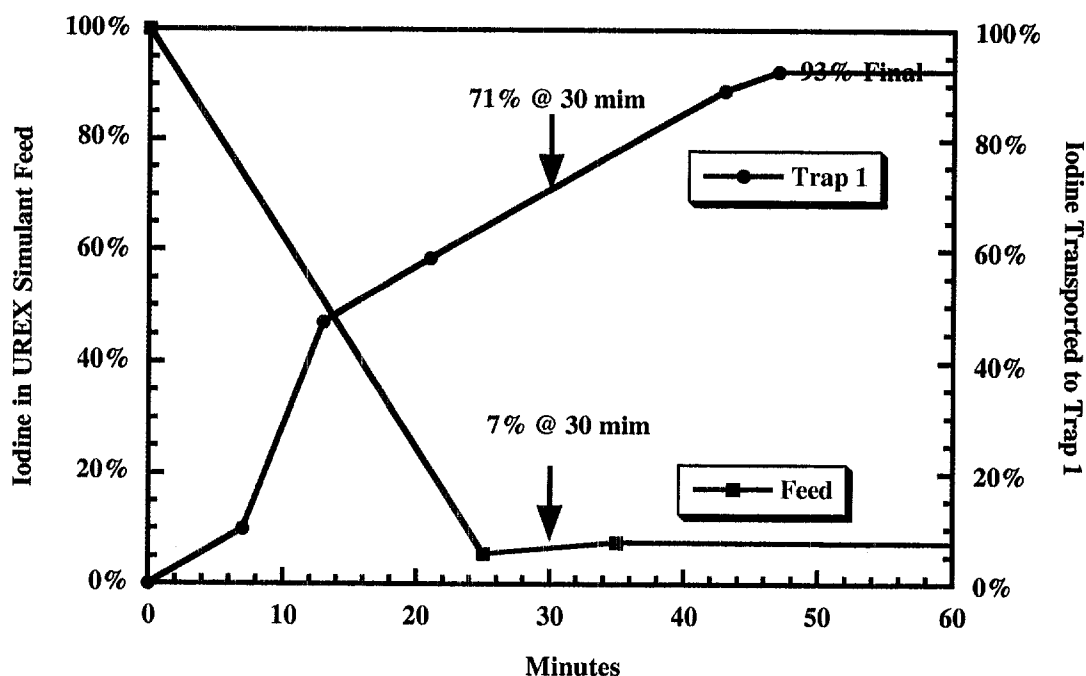


Figure 13. Removal of Iodine from a UREX Feed Solution Simulant (1 M $UO_2(NO_3)_2$ /1 M HNO_3).

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