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HYDRAZOIC ACID CONTROLS AND RISKS WHEN PROCESSING NEPTUNIUM SOLUTIONS IN HB-LINE PHASE II (U)

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Date: 7/31/03

D F Hallman
D. F. Hallman
Author

Date: 7/30/03

J. W. McClard
Technical Reviewer

Date: 7-30-03

J. B. Schaade
Manager, H-Area Technical Support

Date: 7-30-03

W L Isom
W. L. Isom
Manager, HB-Line Engineering

Distribution:
R. M. Mobley, 705-H
D. E. Alexander, 704-2H
P. R. Pritchard, 221-13H
D. W. Murdoch, 221-13H
E. R. Russell, 704-2H
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T. E. Worth, 221-H, HBL
D. M. Cato, 704-2H
J. W. Posnick, 704-2H
J. M. Low, 705-H

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1.0 Summary

Hydrazine mononitrate will be used in processing neptunium in Phase II of HB-Line to scavenge nitrous acid (a byproduct of nitric acid) in the column feed adjustment tank (JT-71 or JT-72) and also in the precipitation feed adjustment tanks (NT-41/42). Nitrous acid can interfere with valence adjustment chemicals (e.g., ferrous sulfamate and ascorbic acid) and thus interfere with controls that give proper neptunium valence. Hydrazine reacts with nitrous acid to form hydrazoic acid, and the hydrazoic acid also reacts with nitrous acid. The concentration of hydrazoic acid can be controlled below the autocatalytic decomposition limit in both liquid and vapor by controlling the maximum concentration of hydrazine mononitrate in the acid solution. The concentration of nitrous acid available for reaction with hydrazine also limits the amount of hydrazoic acid in solution. The hydrazine concentration will be controlled at or below 0.15M in the neptunium solutions to maintain the hydrazoic acid concentration below autocatalytic decomposition limits. Equipment failures and/or human errors that could cause hydrazine to be present above this limit are evaluated. Satisfying the assumptions stated in this report result in a frequency of Beyond Extremely Unlikely (BEU) for a hydrazoic acid autocatalytic decomposition reaction in either the liquid or vapor phase of the process vessels.

2.0 Introduction

The feed solution for neptunium processing in HB-Line Phase II is about 20 grams/liter neptunium in nitric acid solution. This solution is stored in H-Canyon Tank 8.5.

Phase II contains two parallel trains for processing neptunium solutions. Generally, the trains are operated independently. Source terms are calculated based on simultaneous operation of both trains, but this is not planned. Where two equipment designators are used below in parentheses, they refer to equipment in both trains.

For neptunium processing in HB-Line, hydrazine use is planned in the column feed stream and the elutriant stream. Hydrazine is currently not planned to be used in the resin conditioning stream, the decontamination stream, or the precipitation feed adjustment tank. For the purposes of this report, it will be assumed that hydrazine is added to the resin reconditioning stream and the decontamination stream, when the frequency of an autocatalytic reaction due to hydrazine concentration on resin is evaluated. If hydrazine use in these streams is planned for the future at concentrations up to 0.15M hydrazine, the analysis for hydrazoic acid concentration on resin due to errors in addition to the column feed adjustment tank (either JT-71 or JT-72) will not have to be repeated. Additional analyses would be needed for errors in hydrazine addition to these streams, however. An analysis of hydrazine addition to the precipitation feed adjustment tanks (NT-41/42) is included in this report, even though hydrazine use is not planned for these tanks. The hydrazine residual in the elutriant is adequate to protect the valence state of neptunium in these tanks for normal processing. However, if an extended outage occurs while neptunium solution is in these tanks, and it is decided that the material in these tanks need to be recovered to support the campaign objectives, hydrazine addition may be desirable. This report justifies the safety of hydrazine addition to this tank at planned treatment concentrations up to 0.15M, to maintain this option.

Neptunium solution at about 20 grams neptunium per liter will be transferred to JT-71 from Tank 8.5 in H-Canyon. From JT-71, a volume of solution containing about 8000 grams of neptunium will be transferred to JT-72. The nitrate concentration of this solution will be adjusted to ~ 8M and ferrous sulfamate and hydrazine added to adjust the neptunium valence. This solution will then be transferred to column feed tanks and to the ion exchange column. Neptunium and other actinides will be concentrated (not all actinides will be efficiently concentrated) on the resin column. Elutriant will be passed through the resin column to elute a concentrated solution of neptunium and other actinides. The elutriant will contain 0.05M hydrazine for nitrous acid scavenging during eluting and also while the solution is held in the concentrate tank for further processing. This solution, containing high (~ 50 grams/liter) neptunium concentrations is collected in the concentrate tanks (NT-21 and NT-22). Batches of the concentrated solution, containing about 1000 grams of neptunium, are then transferred to the feed adjust tanks (NT-41 and NT-42). This solution is heated to 50 ±5 °C for in preparation for precipitation (Reference 1).

The neptunium solution will then be pumped to the precipitation tanks for precipitation with oxalic acid to form solid neptunium oxalate. A batch of the neptunium solution will first be pumped to the precipitator, then the oxalic acid will be metered into the solution. There is a small nominally four liter first stage precipitation tank (NP-1 and NP-3) that sits on top of a nominally 75 liter second stage precipitator (NP-2 and NP-4). This gives the capability to perform simultaneous feed, two stage precipitation. However, for the neptunium processing campaign, no mixing occurs in this first stage tank, and the valve on the bottom of the tank is fully opened to allow flow into the second stage tank.

The solution in the precipitator tank is stirred until precipitation is complete. This solution, now containing neptunium oxalate solids, excess oxalic acid, and any hydrazoic acid formed, is then vacuum transferred through a filter for solids separation. The liquid flows through the filter into a nominally 100-liter filtrate tank (NT-51 and NT-52). Any hydrazoic acid formed is transported with the liquid into the filtrate tank. The filtration solution will be at approximately 1.3M nitric with the inclusion of the "cake wash 1.4M nitric & 0.1M oxalic" solution used during the filtration step.

Sodium permanganate is then added to the filtrate tank solution. This is added to decompose the oxalic acid excess used to ensure complete precipitation of the neptunium nitrate. It also decomposes the oxalate associated with any solid neptunium oxalate that passes through the filter. The sodium permanganate also oxidizes any hydrazoic acid that is present, and any hydrazine residual that is present. Sodium nitrite is then added, if necessary, to dissolve any manganese dioxide formed from the sodium permanganate addition. Since any hydrazine residual had been destroyed by the permanganate, no hydrazoic acid is formed from the nitrite addition.

3.0 Methods of Analysis

The method of formation of hydrazoic acid while processing neptunium solutions in Phase II of HB-Line is considered in deriving controls to prevent (decrease the frequency of) a hydrazoic acid autocatalytic decomposition. The frequency of a hydrazoic acid autocatalytic decomposition reaction is evaluated considering the failures required to reach conditions where an explosion can potentially occur and the credible locations of a hydrazoic acid autocatalytic decomposition. The controls that reduce the consequences and frequency of a hydrazoic acid autocatalytic decomposition reaction in HB-Line for processing neptunium solutions are identified in the individual evaluations, then summarized in the Assumptions section to enhance ease of identification of the controls.

Background information on the formation of hydrazoic acid, and the mechanism for formation of an autocatalytic decomposition mixture, is discussed further below, to establish the basis for the controls selected to prevent a hydrazoic acid explosion. The methods used to evaluate the frequency of a hydrazoic acid autocatalytic decomposition reaction in Phase II of HB-Line, and the controls to prevent this, are also discussed below.

3.1 Background

The reasons for hydrazine mononitrate usage as a chemical additive are discussed above. Hydrazine mononitrate requires special handling during addition to minimize personnel exposure, but this is a common chemical hazard and is controlled through the WSRC Chemical Control Program (Reference 2) and will not be discussed further in this Technical Report. Hydrazine mononitrate is not a processing hazard except for its contribution to hydrazoic acid formation.

Hydrazine mononitrate reacts with nitrous acid (HNO_2) to produce two molecules of water and a molecule of hydrazoic acid (HN_3), as shown in Equation 1 (Reference 3).

$$HNO_2 + N_2H_4 \longrightarrow HN_3 + 2H_2O \qquad \text{Equation 1}$$

Hydrazoic acid also reacts with nitrous acid to produce water and gaseous products, as shown in Equation 2.

$$HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2O \qquad \text{Equation 2}$$

The equilibrium amount of hydrazoic acid in solution depends on the relative rates of Equations 1 and 2. Laboratory experiments show that, because of the reaction of hydrazoic acid with nitrous acid (Equation 2 above) the maximum equilibrium concentration of hydrazoic acid in liquid is about 25% of the hydrazine concentration. At higher hydrazine concentrations (0.19M and 0.44M) the maximum hydrazoic acid concentration in the liquid was 12% of the hydrazine concentration (Reference 3). In this evaluation, it is conservatively assumed the hydrazoic acid concentration can temporarily be as large as 1/3 the hydrazine mononitrate value. Therefore, if the hydrazine concentration in solution is controlled, the hydrazoic acid concentration is controlled.

It is reported (Reference 5) that solutions must contain at least 30 weight % (~ 8.4M) hydrazoic acid before an explosion can occur in liquid. Therefore, if the concentration of hydrazine used for nitrous acid scavenging is limited below (8.4*3 ~ 25.2M) an explosive mixture in liquid cannot form.

Equation 1 shows that one mole of hydrazine produces one mole of hydrazoic acid and consumes one mole of nitrous acid. The hydrazoic acid then consumes one mole of nitrous acid in Equation 2. From experimental evidence, the ratio of the concentration of hydrazoic acid to hydrazine varies significantly, peaking at 0.25, or ¼. For this evaluation, a ratio of 1/3 is chosen; this is a conservative ratio for this evaluation. Equation 1 shows that one mole of nitrous acid is consumed to produce one mole of hydrazoic acid. Equation 2 then consumes 2/3 of a mole of nitrous acid is consumed to produce 1/3 mole of hydrazoic acid. To 1/3 mole of hydrazoic acid at equilibrium, 5/3 mole of nitrous acid must be consumed. Therefore, five moles of nitrous acid and three moles of hydrazine are consumed per mole of hydrazioc acid that remains in solution.

Hydrazoic acid is relatively volatile (boiling point ~ 37 °C) and is present in the vapor above a liquid solution of hydrazoic acid. Hydrazoic acid may undergo a rapid decomposition in the vapor phase. The partial pressure of hydrazoic acid in the vapor phase where decomposition may occur) is 65 torr (Reference 5). There are 760 torr in an atmosphere; therefore, the volume percent at which hydrazoic acid can decompose is (65/760) ~ 8.5%, or 0.085 atmospheres. The Henry's Law coefficient of hydrazoic acid in water at 30 °C is 0.1 atmospheres vapor/(moles/liter in nitric acid) and is conservatively chosen to be 0.3 atmospheres vapor/(moles/liter in nitric acid) at 60 °C (Reference 6). This coefficient decreases as nitric acid concentration increases and as temperature decreases, so the use of the above bounds the operating conditions. Using a bounding Henry's Law coefficient bounds the vapor phase hydrazoic acid concentration. The amount of vapor phase hydrazoic acid that exists in equilibrium above a hydrazoic acid solution is given by the following equation:

$$y_{HN3} = H_{HN3} * x_{HN3} \qquad \text{Equation 3}$$

Where:

y_{HN3} = partial pressure of hydrazoic acid in vapor phase, atmospheres
H_{HN3} = Henry's Law coefficient for hydrazoic acid, atmospheres/(moles/liter)
x_{HN3} = concentration of hydrazoic acid in liquid phase, moles/liter

The liquid concentration of hydrazoic acid that gives a decomposition partial pressure of hydrazoic acid in the vapor phase is thus (0.085/0.1) ~ 0.85M for tanks at 30 °C and (0.085/0.3) ~ 0.28M in the tanks at 60 °C.

3.2 Frequency Of A Hydrazoic Acid Autocatalytic Decomposition Reaction In The Liquid Phase

HB-Line uses a nominally 30 weight % hydrazine mononitrate [$N_2H_4{\cdot}HNO_3$] solution in water for valence adjustment. This report evaluates a bounding hydrazine concentration in the feed solution of 35 weight % to ensure a bounding value of hydrazine concentration. Conservatively assuming a solution density of 1.021 grams/cc (the density of pure hydrazine), the weight of hydrazine mononitrate per liter is 306.3 grams. In a 35% solution, the hydrazine mononitrate weight would be 357.35 grams/liter. Hydrazine mononitrate has a molecular weight of 95 grams/mole, so the molarity of hydrazine mononitrate in a 35 weight % solution is 3.76M. Per the flowsheet, the hydrazine concentration in the drums is 3.63M, so evaluation at 3.76M is conservative. Decomposition reactions in liquid do not occur below 8.4M hydrazoic acid concentration in the liquid. Since the maximum hydrazoic acid concentration in liquid is 1/3 of the hydrazine concentration, the hydrazine concentration that could lead to a hydrazoic acid autocatalytic reaction is (8.4*3) ~ 25.2M. This molarity cannot be practically attained in solutions treated with hydrazine mononitrate, since the hydrazine mononitrate is diluted by the solution it is added to. Thus the maximum achievable hydrazine concentration is 3.76 M. This is far below the limit of 25.2M hydrazine at which an autocatalytic decomposition concentration of hydrazoic acid in liquid might occur. Therefore, by limiting the hydrazine supply to be added for nitrous acid scavenging to less than 35 weight % hydrazine mononitrate, HB-Line stays about a factor of six below the hydrazine molarity that could cause explosive concentrations of hydrazoic acid in the liquid, even with uncontrolled addition.

The hydrazine mononitrate is contained in drums, and is not hard-piped into the system. There is no mechanism where mechanical failure can cause inadvertent transfer of hydrazine mononitrate from the drums into the process tanks. The only mechanism for adding more hydrazine than planned to the process tanks is human error.

The possibility of hydrazoic acid being retained on the resin column, and eluting as a more concentrated solution when the neptunium is eluted was considered. Hydrazoic acid is a weakly ionized acid; nitric acid is a strongly ionized acid. The azide ions would have to compete with the nitrate ions for resin sites, and the concentration of nitric acid in the column feed is 8M. Since nitric acid is strongly ionized, the concentration of nitrate ions, at this nitric acid concentration, will be high relative to the nitrous acid ions. It is unlikely that a significant amount of azide ion would be retained on the resin. It is also unlikely that any azide ion deposited on the resin would be eluted with the weaker nitric acid solution (0.35M) used to elute the neptunium from the resin. However, tests were run to determine if hydrazoic acid concentrates on the resin (Reference 7). The tests showed no concentration of hydrazoic acid on the resin. However, to conservatively account for measurement uncertainty in the experiment, an analysis was performed assuming that 10% of the hydrazoic acid fed to the resin was retained, and was eluted when the neptunium was eluted. This is analyzed later in this report.

Hydrazoic acid can also concentrate in condensate if the condensing temperature is lower than the evaporation temperature. In HB-Line Phase II, the pertinent condensation point would be the vessel vent system. The vessel vent system is connected to all the Phase II vessels that contain process solutions, and a vacuum is maintained on this system to draw vapors from the vessels for cleanup before discharging the vessel vent system. The concentration of hydrazoic acid in the vapor phase increases as the solution temperature increases, and the concentration in the condensed liquid increases as the condensation temperature is lowered. The hydrazoic acid concentration in condensate in Phase II of HB-Line was evaluated using extreme conditions of evaporation at 50 °C, condensing at 0 °C, and 0.15M hydrazoic acid in the liquid phase (Reference 6). The resulting concentration in the condensing vapor is 1.27M hydrazoic acid. This is also well below the explosive concentration of 8.4M in liquid. This concentration could only practically exist on the walls of vessel vent system piping prior to entry to the vent catch tank. This tank contains about 100 liters of water and would dilute the small amounts of hydrazoic acid transported through the vessel vent system. Further, there is no source term, other than trace levels of radioactivity, in the vessel vent system tubing and tanks, so the consequences of a liquid explosion would be very low. No additional controls will be implemented to control this small risk; controls that make the explosions in process vessel liquid and vapor BEU are adequate to control this small risk.

3.3 Frequency of a Hydrazoic Acid Autocatalytic Decomposition Reaction in the Vapor Phase

Hydrazoic acid can achieve the concentration to undergo a decomposition reaction in the vapor phase if the hydrazoic acid concentration in the liquid phase exceeds 0.85M for tanks at 30 °C and 0.28M in the tanks at 60 °C. It is conservatively assumed that the concentration of hydrazoic acid in the liquid phase can be as high as 1/3 of the hydrazine concentration, if the nitrous acid supply is sufficient to support this amount of hydrazoic acid being created. Therefore, if the hydrazine concentration is kept less than (0.85*3) ~ 2.55M in tanks with temperatures 30 °C or less, or (0.28*3) ~ 0.84M in tanks with 60 °C or less, the concentration in the vapor phase of these tanks will be less than the decomposition concentration.

4.0 Analysis and Results

As stated above, the frequency of a hydrazoic acid decomposition event in liquid is BEU if the hydrazine mononitrate feed solution is 35% or less (by weight) hydrazine mononitrate. The frequency of hydrazoic acid decomposition reactions in the vapor phase from treating neptunium streams with hydrazine is evaluated below.

4.1 Column Feed Adjustment in JT-72

Hydrazine is added to the solution in JT-72 to assist in valence adjustment in the column feed solution. Two methods of adding hydrazine are considered, and both are evaluated here to ensure the frequency of achieving a decomposition reaction in the vapor phase of the tanks involved is BEU.

The flowsheet (Reference 1) specifies treating the column feed solution to achieve 0.02M hydrazine. This report will evaluate a treatment concentration of 0.15M hydrazine for additions to JT-72. This will provide operational margin in case it is found desirable to increase the hydrazine concentration in this stream in the future, and to provide a bounding limit for the analysis.

This analysis also assumes that the column reconditioning stream, decontamination stream, and elution stream are treated to 0.15M hydrazine. Currently, no hydrazine addition is planned for the reconditioning and decontamination streams. It is included in this analysis to allow treatments up to those concentrations in the future without having to repeat the analysis of hydrazine additions to the column feed and precipitator feed tanks.

The volumes of solutions that could add hydrazoic acid to resin assumed for this portion of the analysis are from the flowsheet (Reference 1). They are summarized below.

Table 1: Volumes of Solution Added to Resin for a 2000 Gram Loading

Stream	**Column Reconditioning**	**Column Feed**	**Decontamination Wash**
Volume, Liters	45	208	91

The volumes of the elutriant streams used are summarized below These volumes are from Reference 1.

Table 2: Volumes of Solution in Elution Streams for a 2000 Gram Elution

Stream	**Heads Cut**	**Hearts Cut**	**Tails Cut**
Volume, Liters	45	36.1	91(once per 4 column runs)

4.1.1 Hydrazine Mononitrate Addition to JT-72 Using Funnel Valves in Room 410

The design of the JT-71/JT-72 tank system includes the ability to add chemicals through funnel valves that feed into intermediate tanks, then into the primary tanks. There is a possibility this mechanism will be used, so it is evaluated in this report.

From the flowsheet, the amount of solution transferred to JT-72 for treatment is 832 liters. Tank JT-72 has a 300-liter heel. The total amount of solution to be treated is then 1132 liters.

It is assumed the heel starts with no hydrazine. This is a conservative treatment for this analysis. If there is a hydrazine residual in the heel, there is no nitrous acid to react with additional hydrazine that is added. Therefore, no hydrazoic acid would be produced from the hydrazine added to adjust the heel volume. It is therefore conservative to assume there is nitrous acid present in the heel for the purposes of this analysis.

The volume of hydrazine to be added to achieve a final concentration of 0.15M is calculated from Equation 4:

$$\text{Volume} = V_{St}*C_{Final}/(C_{Add}-C_{Final}) \qquad \text{Equation 4}$$

Where:
Volume = volume of treatment chemical to be added, liters
V_{St} = Volume of solution before adjustment, liters
C_{Add} = Concentration of treatment chemical stream, moles/liter (3.76M for this analysis)
C_{Final} = Concentration in final treated solution, moles/liter

Including the heel, the volume of solution to be treated is 1132 liters. The target hydrazine concentration is 0.15M, for purposes of this analysis. Applying Equation 4, the volume of hydrazine to be added is ~ 47 liters.

If 10% of the hydrazoic acid is retained on the resin, there are 8.56 moles of hydrazoic

Reference 8 documents an evaluation of the probability that enough hydrazine would be added to Tank JT-72 to cause an autocatalytic decomposition reaction in either the JT-72 tank liquid, the JT-72 tank vapor space, or the concentrate tank when the neptunium is eluted from the resin. The limiting case is elution from the resin.

A series of tests were performed to determine if hydrazoic acid could be concentrated by the ion exchange resin during processing. The report (Reference 7) concluded that there will be no concentration of hydrazoic acid on the resin. This is as expected. Nitric acid is a strong acid and will ionize readily. Hydrazoic acid is a weak acid and does not readily ionize. There will be a large number of nitrate ions competing for resin exchange sites with a small number of azide ions. Also, if any azide ions adhere to the resin in a 8M nitric acid solution, they are unlikely to be displaced from the resin with a weak elutriant (about 0.17M nitrate). However, for purposes of this report, it was assumed that 0.1 (10%) of the hydrazoic acid fed to the resin column adhered to the column, and was eluted in the hearts cut containing the neptunium. This accounts for potential uncertainties in the experiment. Therefore, Reference 8 assumes 10% of the hydrazoic acid adheres to the resin from the resin reconditioning step, the resin feed step, and the resin decontamination step.

Reference 8 concludes that a hydrazoic acid autocatalytic decomposition reaction due to human errors during hydrazine addition to JT-72 is BEU, and that it would take ~ 20 human errors to reach this concentration. The initial volume of neptunium solution in JT-72 is 832 liters of process solution plus a 300-liter heel. About 3704 moles of hydrazine would have to be added to JT-72 to reach the autocatalytic decomposition concentration.

The temperature in JT-72 could be slightly above ambient due to the addition of 14M acid to the process solution to raise the nitrate concentration of the solution. The Henry's Law coefficient of 0.1 atmospheres/(moles/liter) is for 30 °C in water, per Table 1 of Reference 6, and this value was used in the JT-72 analysis. This table also shows that the Henry's Law coefficient decreases as the nitric acid concentration in the solution increases. The JT-72 solution is adjusted to ~ 8M nitric acid. The effect of the higher nitric acid concentration in JT-72 will compensate for the effect of any small increase of temperature above 30 °C.

Although the analysis was performed assuming JT-72 is the tank where the column feed solution is adjusted, the results would be identical had JT-71 been used as the column feed adjustment tank.

Therefore, the number of human errors required to achieve this concentration in JT-72 makes the frequency of the event BEU.

4.1.2 Hydrazine Mononitrate Addition to JT-72 Using Cold Feed Prep

The planned way of adding the hydrazine to JT-72 is by adding it to the Cold Feed Prep tank used to add the high-molarity acid needed to adjust the JT-72 solution to 8M nitrate. These are tanks CP-24 or CP-25. The flowsheet (Reference 1) shows 352 liters of nitric acid added to JT-72. Solution is pumped from these tanks through an eductor with the eductor suction valve closed for transfer to JT-72. The pump is automatically cut off when the level reaches an indicated level of 3%. This is about 74 liters for CP-25 (higher for CP-24). The 352 liters of nitric acid is added to this existing level, to give a level of 426 liters.

The tanks contain a 2-inch overflow port (Reference 9). The centerline of this overflow port is four inches from the top of the tank (Reference 10). The upper cylindrical portion of the tank is 36 inches OD with a 3/16-inch wall (Reference 10). The volume of the top four inches of the tank is 65.28 liters. The tank is nominally 600 liters, but was measured at 636 liters (Reference 10). The volume of the tank below the overflow port centerline is thus (636-65) ~ 571 liters. The volume that can be occupied by liquid is thus (571 – 426) ~ 145 liters. This is the maximum volume that the tank would hold of hydrazine.

These tanks have both a high-level alarm and a high-high level alarm below the overflow point. To reach the overflow point, both alarms would have to be ignored by the personnel doing the additions and personnel in the control room. Continued additions after the alarm setpoint is reached are unlikely, even though assumed in this analysis.

If, through human error, only 75% of the planned nitric acid volume is added to the tank, more hydrazine could be added before reaching the overflow. The volume available in the tank would be (571 – 0.75*426) ~ 252 liters. Moles of hydrazine added would be (3.76*252) ~ 948 moles. The hydrazine molarity in the addition tank would be (948/571) ~ 1.66M. The hydrazoic acid molarity would be (1.66/3) ~ 0.554M. This is far below the 8.4M concentration in liquid where an autocatalytic decomposition reaction occurs. The vapor concentration is (0.554*0.1*760) ~ 42 torr, which is below the 65 torr at which an autocatalytic decomposition reaction in vapor occurs.

. The analysis in Reference 8 concluded that an autocatalytic decomposition would not occur if 3704 moles of hydrazine were added to JT-72. This is far above the amount of hydrazine that would be added to the overflow point as stated above, even if only 75% of the nitric acid required were added to the cold feed tank.. Therefore, when CP-24 or CP-25 is used to add hydrazine to JT-72, the physical configuration of the tank does not allow enough hydrazine to be added to cause a decomposition reaction for hydrazoic acid. This is true for JT-72 and also for the concentrate tanks (NT-21/22) even if it is assumed that 10% of the hydrazoic acid concentrates on the resin bed and is eluted with the hearts cut.

The hydrazine solution is probably miscible with nitric acid, so additions after the overflow point are reached would mix somewhat with the solution in the tank before overflowing. This could cause a slow concentration increase in the hydrazine concentration in the 600-liter tanks. This is not a significant factor for this analysis. The conservative assumption that the concentration of hydrazoic acid can be 1/3 of the hydrazine concentration, rather than the maximum concentration of ¼ shown by the data, more than compensates for the slow increase of hydrazine concentration that would occur during tank overflow.

4.2 Hydrazine Mononitrate Addition to the Resin Elutriant Solution

Hydrazine is added to the elutriant (the stream that elutes the neptunium from the resin bed). The flowsheet (Reference 1) specifies a concentration of 0.17M nitric acid for elutriant. This analysis bounds the nitric acid concentrations in the elutriant from process water (essentially 0 molarity) to the maximum molarity solution (about 4M) that can be expected to elute neptunium from the column.

It is planned to use Tank CE-23 (CN-23) to contain the elutriant solution, but this analysis applies to tanks CE-22, CP-24, and CP-25. All these tanks are as described in Reference 10. This analysis uses the level in the tank at the indicated level of 3% as an input. Of the four tanks, CE-23(CN-23) contains the lowest solution volume at 3% indicated level (Reference 14). This volume is 69.87 liters. Choosing the tank with the lowest volume is conservative for this evaluation.

Further, the current flowsheet (Reference 1) specifies a heads cut of 45 liters and a hearts cut of 36.1 liters per column run, with a single tails cut of 91 liters after four column runs. This is with current goals of efficiency for the column loading and eluting, and assuming the resin columns will hold 45 liters of resin. This analysis will consider multiple erroneous additions of hydrazine to the elutriant tank. It will show that the tank cannot hold sufficient hydrazine to generate hydrazoic acid at autodecomposition concentrations. Therefore. lower volumes of elutriant bound the values currently in Reference 1. If a

1500 gram batch were to be processed through the resin column, the volumes for the heads cut, and hearts cut, would probably decrease to the values shown in Table 4 below. The values chosen for a bounding analysis are shown in Table 4 below.

Table 3: Elutriant Solution Volumes

Elution Step	Volume per cycle, liters	Volume for four column runs, liters
Head Cut	35.3	130
Hearts Cut	35.3	152.8
Tails Cut	91	91
TOTAL		**373.8**

Per Reference 10, these tanks have a volume of 636 liters, even though they are nominally known as 600 liter tanks. The tanks also have a 2-inch overflow port; the centerline of this port is four inches below the top of the tank. The tanks are 36 inches outside diameter with a 3/16-inch wall thickness. The volume from the top of the tank to the centerline of the overflow port is:

$(\pi/4)((35.6125)^{\wedge}2\text{in}^2)(4 \text{ in high})(0.01639 \text{ liters/in}^3) \sim 65.28$ liters

So, the total volume of the tank to the overflow centerline is (636 – 65) ~ 571 liters.

As previously stated, the tank with the lowest liquid level at the 3% pump cutoff contains 68 liters at that point. The remaining volume in the tank to the centerline of the overflow port is (571 – 69) = 502 liters. The elutriant solution will occupy ~ 373 liters, so there will be only (502 – 373) = 129 liters. If, through human errors, multiple additions of hydrazine occur, the maximum amount of hydrazine mononitrate that can be added to the tank is 129 liters; the passive tank overflow limits the volume of hydrazine mononitrate to this amount. At 3.76M concentration, the maximum moles of hydrazine that can be added is (3.76x129) ~ 485 moles of hydrazine mononitrate. The tank liquid volume is (485/571) ~ 0.85M concentration of hydrazine mononitrate. The maximum concentration of hydrazoic acid for this hydrazine concentration is (0.85/3) ~ 0.283M. This is much less than the 8.4M concentration for autocatalytic decomposition in liquid.

The elutriant tank and elutriant solution are at room temperature, so the Henry's Law coefficient is 0.1 atmospheres/(moles/liter). The concentration of hydrazoic acid in the vapor space is (0.283x0.1x760) ~ 22 torr. This is well below the autocatalytic decomposition partial pressure of 65 torr.

These tanks have both a high-level alarm and a high-high level alarm below the overflow point. To reach the overflow point, both alarms would have to be ignored by the personnel doing the additions and personnel in the control room. Continued additions after the alarm setpoint is reached are unlikely, even though assumed in this analysis.

If only 75% of the required elutriant volume is added to the 600-liter tank, the volume of liquid in the tank would be (502 – 0.75*373) ~ 222 liters. The moles of hydrazine that could be added to the overflow point is (3.76*222) ~ 835 moles. This is less than the 948 moles assumed to be added to the 600-liter tank in Section 4.1.2 of this report. Therefore, the conclusions reached in Section 4.1.2 that this would not result in an autocatalytic decomposition in either liquid or vapor also apply here.

After the overflow point is reached, there would be some mixing of the added hydrazine solutions with the solution already in the tank, so the hydrazine concentration in the tank would slowly increase. This is not a significant factor for this analysis. The conservative assumption that the concentration of hydrazoic acid can be 1/3 of the hydrazine concentration, rather than the maximum concentration of ¼ shown by the data, more than compensates for the slow increase of hydrazine concentration that would occur during tank overflow.

Since the passive overflow prevents addition of enough hydrazine to reach autocatalytic decomposition concentrations in either liquid or vapor phase, the frequency of a hydrazoic acid explosion as a result of human errors when adding hydrazine to the elutriant solution is BEU.

4.3 Hydrazine Mononitrate Addition to the Precipitator Feed Adjust Tank

Adjustment chemicals are added, as necessary, to the feed adjust tank (NT-41/42) to ensure proper precipitation. The flowsheet (Reference 1) assumes no chemical addition will be needed, unless solutions are left in the feed adjust tank for greater than two weeks before precipitating. It assumes there will be sufficient residual hydrazine in the eluted solution to preclude the need for more additions. Because of the potential problems with ascorbic acid use , it is more likely that aged solutions awaiting precipitation would be discarded rather than precipitated. However, as stated earlier in this report, the effects of adding hydrazine to NT-41/42 will be analyzed here to preserve the option of future addition.. For this analysis, it will be assumed that hydrazine is added to NT-41/42 to achieve a concentration of 0.15M.

NT-41/42 can hold about 77 liters of solution (Reference 11). It will receive about 26 liters of solution, at a nitric acid concentration of about 2.3M (Reference flowsheet), from the concentrate tank.

Human errors and instrument failures were considered for evaluation. The following scenario was assumed:

- The digital control system (DCS) fails such that an 8M nitric acid solution (such as used for the decontamination wash or column reconditioning) is fed downflow rather than upflow.

- The colorimeter fails in a way that diverts this solution to the concentrate tanks (NT-21/22).

- A person either fails to take a sample of these tanks, or misinterprets the sample results, and transfers 26 liters of 8M solution to the feed adjust tank (NT-41/42).

- A person adds the amount of hydrazine calculated for addition to JT-72 to NT-41/42.

The above errors were not analyzed for frequency to ensure they are BEU. Instead, the basic chemistry of nitrous acid in nitric acid was considered. Nitrous acid is a byproduct in nitric acid; it can be formed by radiation or light. The nitric acid is stored and blended in metal tanks, so it is only incidentally exposed to light. In the scenario that results in high molarity (8M) nitric acid in the feed additive tank, there would be very little radioactive material in the solution because the radioactivity will not elute from the column at this molarity. Further, the neptunium solutions contain fewer curies than do plutonium solutions, due to the long half-life of neptunium –237 (2,144,000 years) the energy emission rate is much less than for plutonium solutions. The energy emission rate is about three orders of magnitude lower for the neptunium solutions in H-Canyon Tank 8.5 than for heat source solutions encountered in the past. The nitrous acid formation rate will be low for the neptunium solutions.

Hydrazine is typically stable in nitric acid, and does not react significantly even at the bounding temperature of 60 °C assumed for NT-41/42 (Reference 12). Typical nitrous acid concentrations are in the ppm range.Levels up to 1% of the nitrate concentration without the addition of nitrite ions from an external source would be significantly higher than expected (Reference 13). For this evaluation, a bounding nitrous acid concentration of 10% of the nitrate concentration is assumed. From previous discussions, formation of one mole of hydrazoic acid consumes at least 5 moles of nitrous acid, so the maximum amount of hydrazoic acid formed is calculated by calculating the number of moles of nitrous acid present and dividing by 5. This is (8M HNO_3*0.1HNO_2/HNO_3*26 liters/5) ~ 4.16 moles HN_3. Three moles of N_2H_4 are needed per each mole of HNO_2; this is (4.16*3) ~ 12.48 moles. This requires (12.48 moles N2H4/3.76 moles N_2H_4/liter) ~ 3.3 liters of N_2H_4 solution. The hydrazoic acid concentration of the final solution is 4.16 moles/(26 + 3.3 liters) ~ 0.142M. Applying Equation 3 with a Henry's Law coefficient of 0.3 atmospheres/(moles/liter), the partial pressure of hydrazoic acid in the vapor space is ~ 32 torr. This is significantly less than the 65 torr for the decomposition reaction in vapor. Therefore, an autocatalytic reaction in the feed additive tank is BEU.

5.0 Assumptions

1 The volumes of solutions used for this evaluation assume that four consecutive column runs of about 2000 grams each are made, and a tails cut is used only at the end of the fourth run.

2 The maximum strength of hydrazine mononitrate used for feed adjustment is 3.76M. The site plans to purchase 3.63M hydrazine mononitrate.

3 The amount of hydrazine to be added to a tank will be specified by procedure.

4 Hydrazine must be manually transported to the addition stations. HB-Line will not include a hard-piped system from the hydrazine source to the hydrazine addition point.

5 The neptunium solution now in H-Canyon Tank 8.5 is the only solution that will be processed using the conclusions of this report, without further evaluation to ensure the conclusions are still valid.

6 The maximum hydrazine concentration that will be specified by procedure for treatment of a process stream is 0.15M.

7 The elutriant stream will be made up in one of the 600-liter tanks (now designated as CE-22, CE-23, CP-24, or CP-25).

8 If hydrazine is added for the column adjustment stream in Cold Feed Prep, the column adjustment stream will be made up in one of the 600 liter tanks discussed in Assumption 6.

6.0 Discussion

In this analysis, bounding assumptions are typically chosen to ensure the conclusions are robust. The use of a 1:3 ratio of hydrazoic acid to hydrazine, and a concentration of 3.76 molar hydrazine for treatment, are examples of this conservatism. Minor changes in other assumptions used are unlikely to change the conclusions of this report.

7.0 Recommendations

It is recommended that the assumptions made in arriving at the conclusion that an autocatalytic decomposition of hydrazoic acid is BEU be implemented in HB-Line.

8.0 References

1. CBU-HCP-2003-00044, Rev. 0, *HB-Line Np-237 Flowsheet*, March 14, 2003

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4. DP-808, "*Uranium(IV) Nitrate as a Reducing Agent for Plutonium(IV) in the Purex Process,*" April 1963

5. SRT-ATS-2001-00003, *Literature Search and Review of the Hazards of Hydrazoic Acid*, Jan. 10, 2001

6. X-CLC-H-00146, *Condensate Hydrazoic Acid Concentrations for Vapor from HB-Line Process Solutions*, January 12, 2001

7. WSRC-TR-2003-00015, Rev. 0, *Absorption of Hydrazoic Acid on Reillex^{tm} HPQ Anion Exchange Resin*, February 2003

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9. W718118, Rev. 74, *Cold Feed Prep P&I Diagram, Partitioning Tanks, Process and Instruments*

10. BPF 213457, Sheet 3, *Vertical Tank*

11. PV180694, Rev. 11, *75 Liter F/A Tank*

12. Karraker, David G., *Oxidation of Hydrazine by Nitric Acid*, Inorg. Chem. 1985, 24, 4470-4477

13. Private Communication with David Karraker, SRTC, 7/18/03

14. FRM 221-HB-900D, Rev. 1, *Cold Feed Prep 2 Calibration Charts*, 3/26/03