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Solvent Recovery and Management at the Savannah River Site H-Canyon Facility

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EXECUTIVE SUMMARY

NIOWAVE, Inc. is a domestic supplier of medical and industrial isotopes from uranium and radium. The Savannah River National laboratory (SRNL) is currently providing support to NIOWAVE, which plans to deploy a superconducting electron linear accelerator (LINAC) to fission uranium for Mo-99 production without the need for a nuclear reactor or HEU. The uranium from the Mo-99 production targets will be purified using a modified PUREX (Plutonium Uranium Reduction Extraction) solvent extraction process to recover the uranium in the product stream. The uranium will then be precipitated as an oxalate which is calcined to U_3O_8 to fabricate pellets for new Mo-99 targets.

In previous support provided to NIOWAVE, the SRNL demonstrated a solvent washing process to remove degradation products from the tributyl phosphate (TBP) solvent used in the modified PUREX process under development for uranium recovery. To supplement this technology demonstration, NIOWAVE requested the SRNL to provide summary information on the solvent recovery and management activities which are used at the Savannah River Site (SRS) H-Canyon facility. An existing reference document for the reprocessing of irradiated HEU fuels at the SRS was used as the primary reference for the solvent management activities; although, other reference documents were used to provide supplementary information.

The information provided includes a brief summary of the solvent degradation issues which have been observed in the H-Canyon solvent extraction cycles and resulting process safety concerns. The solvent recovery processes for the three cycles of solvent extraction used in the H-Canyon were subsequently described including the process equipment which consists of the continuous and batch solvent washers, pumps, and tanks. A final section is provided on the monitoring and analysis of solvent quality based on the previous work performed at the SRNL for NIOWAVE and past research and development activities performed to support the solvent extraction processes in both the SRS F-Canyon and H-Canyon facilities.

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DBP	dibutyl phosphate
HEU	highly enriched uranium
LINAC	superconducting electron linear accelerator
MBP	monobutyl phosphate
NMR	nuclear magnetic resonance
PDC	polarographic diffusion current
PUREX	Plutonium Uranium Reduction Extraction
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	tributyl phosphate

1.0 Introduction

NIOWAVE, Inc., is a domestic supplier of medical and industrial isotopes from uranium and radium. The company is engaged in a cooperative agreement with the U.S. Department of Energy's National Nuclear Security Administration (NNSA) to produce Mo-99 without the use of highly enriched uranium (HEU). The United States currently produces very little Mo-99 and, therefore, imports essentially all of its supply from foreign producers. The continuity of the Mo-99 supply has also been an issue in the past. Aging infrastructure and planned and unplanned outages of reactors used to produce Mo-99 have resulted in supply interruptions. NNSA's support to the cooperative agreement participants is based on a 50% government/50% commercial cost-share basis.[1] In addition to the financial support provided directly to the commercial businesses, NNSA has also funded national laboratory support to assist in the commercialization of the Mo-99 production processes. The Savannah River National Laboratory (SRNL) is currently providing support to NIOWAVE, which plans to deploy a superconducting electron accelerator (LINAC) to fission uranium for Mo-99 production without the need for a nuclear reactor or HEU.[2]

The NIOWAVE production process for Mo-99 uses U_3O_8 pellets as the target material in the LINAC. Molybdenum-99 is one of the predominate uranium fission products generated during pellet irradiation. After cooling for nominally one day, the pellets are dissolved in nitric acid to prepare a feed solution for the purification and recovery of the uranium. The uranium is purified using a modified PUREX (Plutonium Uranium Reduction Extraction) solvent extraction process designed to recover the actinides in the uranium product stream, shown in Figure 1-1. The modified PUREX process utilizes a 30 vol % tributyl phosphate (TBP) in dodecane as the solvent. The Mo-99 is not extracted by the TBP solvent and is rejected to the raffinate. The raffinate is subsequently processed for the recovery of the Mo-99 and other isotopes of interest. The uranium in the product solution from the PUREX process is precipitated as an oxalate which is calcined to U_3O_8 for pellet fabrication.

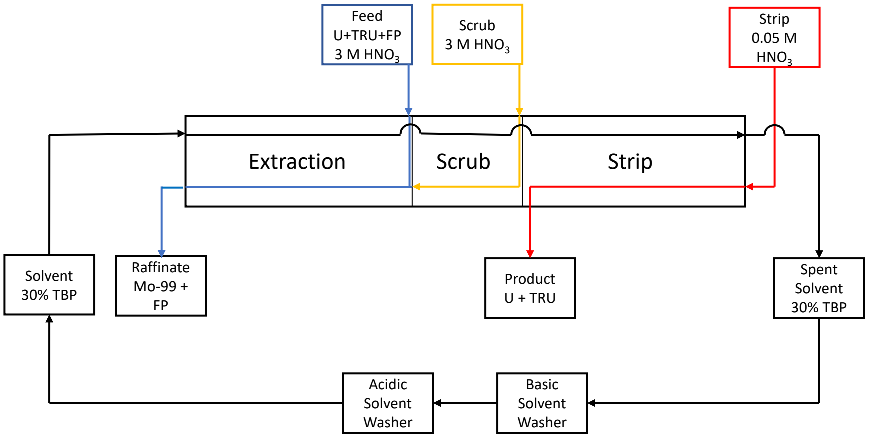

Figure 1-1. Modified PUREX Process for Recovery of Uranium from NIOWAVE Mo-99 Targets

In previous support provided to NIOWAVE, the SRNL completed a demonstration of a solvent washing process to remove degradation products from the TBP solvent used in the modified PUREX process under development for the recovery of U from Mo-99 production targets.[3] To supplement this technology demonstration, NIOWAVE requested SRNL to provide a summary of the solvent recovery and management activities which are used at the Savannah River Site (SRS) H-Canyon facility. An existing reference document for the reprocessing of irradiated highly enriched uranium (HEU) fuels at the SRS was used as the primary reference for the solvent management activities; although, other reference documents were used to provide supplementary information. The information provided in the following sections includes a brief summary of the solvent degradation issues which have been observed in the H-Canyon solvent extraction cycles and resulting process safety concerns. The solvent recovery processes for the cycles are subsequently described including the process equipment which consists of the continuous and batch solvent washers, pumps, and tanks. A final section is provided on the monitoring and analysis of solvent quality based on the previous work performed at the SRNL for NIOWAVE and past research and development activities performed to support the solvent extraction processes in both the SRS F-Canyon and H-Canyon facilities. The solvent recovery systems and equipment described were based on a reference document which was issued in the late 1970s. Some minor modifications to the H-Canyon processes and equipment have been made since that time; however, the information provided is still a good description of solvent management and recovery processes which maintained the quality of the solvent systems used in the H-Canyon facility for many years.

2.0 Solvent Management

2.1 General

The SRS H-Canyon facility has historically been used for the dissolution and purification of HEU fuels and the recovery and purification of transuranic isotopes such as Np-237 and Pu-242. The processing equipment in the canyon includes three cycles of solvent extraction. Two cycles (1st Cycle and 2nd U Cycle) are used for the reprocessing of HEU fuels from foreign and domestic research reactors. The remaining cycle was used as a second product cycle on a campaign basis primarily for further purification of Np-237. Each of the solvent extraction cycles utilizes an independent solvent system. The 1st Cycle and 2nd U Cycle utilize 7.5 vol % TBP in a normal paraffin (C-12 to C-14) hydrocarbon to limit the concentration of HEU extracted into the solvent. The Second Product Cycle utilized 30 vol % TBP in a normal paraffin hydrocarbon like the PUREX process.

The solvent from each extraction cycle also has a separate recovery system. The solvent recovery process is used to remove deleterious materials, degradation products, and radioactive contaminates from the spent solvent and to return the treated solvent to the extraction process in a uniform and standard composition. If allowed to accumulate, the contaminants would adversely affect decontamination, product recovery, and production capacity of the solvent extraction cycle. Any stagnant solvent is collected periodically and isolated for special disposal. The solvent from each extraction cycle is treated continuously with sodium carbonate and nitric acid (or acidified process water). The sodium carbonate removes most of the contaminates and degradation products, and the nitric acid neutralizes any residual alkalinity and enhances the clarity of the purified solvent.[4]

2.2 Solvent Degradation

During the operation of the H-Canyon solvent extraction processes, the solvent accumulates both radioactive and nonradioactive contaminants, which reduces its effectiveness and renders the solvent unsuitable for immediate reuse. The principal radioactive contaminants in the SRS cycles include zirconium, niobium, and ruthenium. Small amounts of uranium or neptunium may also be present. Radioactive iodine is a potential contaminant, but I-131 decays rapidly and no problems have been encountered when processing fuels and targets which have been sufficiently cooled.[4] However, if short-cooled targets are processed for uranium recovery, the diluent can react with iodine. Iodine is an excellent scavenger for hydrocarbon free radicals producing alkyl iodides from the radioactive iodine. Therefore, it is desirable to use only diluents of the highest purity with respect to reactive functional groups such as "unsaturation sites" which pickup iodine.[5] The nonradioactive contaminants produced during the reprocessing of fuels or targets include the hydrolysis products of TBP and various oxidation and nitration products of the hydrocarbon diluent.[4]

The most prominent degradation product generated from the use of TBP for purification of uranium by solvent extraction is dibutyl phosphate (DBP).[6] Dibutyl phosphate is produced both by chemical damage (hydrolysis) and by radiation damage, with the relative amounts depending on the specific activity of the radioactive solution processed. Dibutyl phosphate is readily removed by alkaline washing and does not tend to accumulate in the solvent during successive passes through the solvent extraction cycle. Dibutyl phosphate is preferentially soluble in the organic phase and forms strong complexes with zirconium, uranium(VI), and plutonium(IV). The complex with zirconium causes zirconium to be extracted along with the uranium in the solvent extraction process.[7] Some of this zirconium is released to the aqueous product streams during solvent stripping which restricts decontamination. Dibutyl phosphate also forms solid compounds with aluminum and iron. These solids tend to accumulate at the liquid interface in the H-Canyon mixer-settlers and promote emulsion formation. Both monobutyl phosphate (MBP) and DBP also form strong complexes with neptunium and cause losses to the solvent. These complexes eventually reach the H-Canyon solvent washes and are decomposed for neptunium recovery there by boiling which degrades the MBP and DBP. Contacting the solvent with weak acid will not extract the neptunium in the presence of MBP and DBP.[4]

Degradation products formed from the diluent are not as pronounced in the H-Canyon HEU solvent extraction process as the degradation products formed during the operation of the PUREX process. As a result, the residual fission product activity and contaminant concentrations are much lower in the H-Canyon process solvent than in PUREX solvent. The lower damage to the diluent is attributed to: (1) a lower nitric acid concentration is required in the first cycle due to aluminum from the dissolved fuel, (2) no nitrite addition is required for uranium recovery, and (3) a lower concentration of TBP is used which limits extraction of nitrous and nitric acid and fission products into the organic phase. Many of the degradation products produced from the diluent resist removal in the normal solvent washing operations and tend to accumulate in the solvent. These compounds cause zirconium to extract and follow the uranium product during purification. Also, some of the activity remains in the solvent even after washing and causes undesirable radiation during solvent storage. These degradation products, which act as complexing agents, are associated with the solvent, and may include ketones, diketones, esters, and their polymers. They are formed mainly by exposure of the solvent to nitrous-nitric acid solutions and radiation fields. The formation of these compounds is relatively rapid above 50 °C.[4]

The Second Product Cycle solvent, which utilizes 30 vol % TBP and is in contact with higher HNO_3 concentrations, normally has the highest residual fission product activity of the three H-Canyon solvent systems. Other solvent degradation products cause loss of uranium or neptunium to the spent solvent, affect phase disengagement, and impart a yellow color to the diluent.[4]

Analytical tests have been developed to measure the degree of solvent degradation during uranium recovery operations. Two methods, which are no longer used, include the measurement of the polarographic diffusion current (PDC) and an empirical test based on equilibrating the degraded solvent with a zirconium tracer solution of known activity and concentration. Both tests were used as indicators for possible disposal of solvent. The diffusion current is a relative measure of the gross amount of degradation products and was used as a yardstick for solvent quality. The diffusion current for virgin solvent is zero amp/mL.[4] A zirconium retention number was calculated from counting the residual beta activity in the solvent following Zr extraction and a prescribed nitric acid strip.[8] Disengagement time was also historically used to evaluate solvent quality. The disengagement time is the time required for the organic and aqueous phases to completely separate immediately after mixing. However, the test was generally abandoned in favor of interfacial tension measurement due to the subjectivity involved and difference in perspective between operators.[3] The interfacial tension is a measure of the surfactant concentration which affects the hydraulic properties of the solvent, including phase disengagement time and emulsion formation. Initially interfacial tension of the solvent was measured using 0.7 M NaOH, but was later changed to 2.5 wt % sodium carbonate based on recommendations by Reif.[9] Additional information on interfacial tension measurement is provided in Section 2.6.2 of the report. It should also be noted that some solvent has demonstrated good extraction properties even though the quality measurements were poor. The main indicator for disposal of solvent is poor extraction properties or phase separation as determined by its use, that is, how well the process performs.

2.3 Solvent Recovery

The solvent from each of the three H-Canyon solvent extraction cycles has a separate recovery system. The solvent in each system is segregated from solvent used in the other extraction cycles. This segregation aids in meeting the purity specifications for the final product solutions. Although most of the solvent from the process is washed immediately, floating solvent heels accumulate in the aqueous run tank decanters. This solvent may become seriously degraded and is discarded as waste.[4]

The spent solvent streams from the 1st Cycle and the 2nd U Cycles are washed continuously with sodium carbonate and then transferred outside of the H-Canyon building for washing with dilute nitric acid or acidified process water. As the process solvent inventory decreases due to losses, new solvent is added at the carbonate washer of the appropriate system. The new solvent is washed along with spent solvent to remove impurities such as DBP, MBP, phosphoric acid, and butanol present in the fresh TBP. Washed solvent is sent to storage tanks for subsequent use. The spent carbonate wash solutions of the 1st Cycle and the 2nd U Cycle solvent washers are replaced every 7 to 14 operating days. The spent acid wash solutions are replaced every 5 to 8 operating days. The replacement of the carbonate and acid wash solutions is generally based on the continuous operation of the 1st and the 2nd U Cycles. If the activity level of the solvent is excessive, the wash solutions are replaced more frequently.[4]

The first cycle spent solvent is pumped continuously from the mixer-settler banks to a hold tank and is washed with about 15,000 lb of 2.5 to 5.0 wt % sodium carbonate in the first of two identical continuous washers (Figure 2-1). The solvent is contacted with an equal quantity of sodium carbonate solution in the second washer for further removal of degradation products and contaminants. Sodium carbonate is used

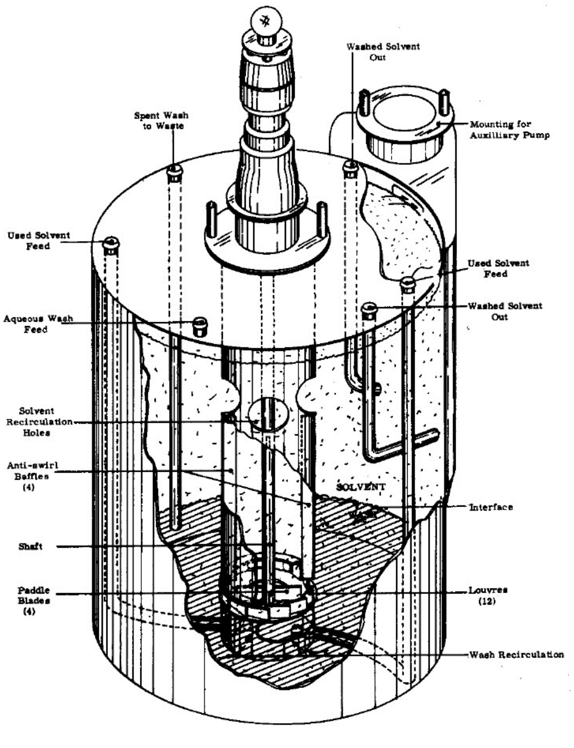

Figure 2-1. Continuous Solvent Washer

in both washes to minimize the possibility of precipitating HEU. The washing temperature is usually controlled in the range of 45 to 50 °C. A higher temperature (at the tank hot water coils), is not used because of the relatively low flash point of the solvent vapor (see Section 2.4 on process safety). The alkaline-washed solvent is pumped outside the H-Canyon building for continuous washing with about 20,000 lb of 0.63 wt % nitric acid and flows to the 1st Cycle washed solvent hold tank. The spent sodium carbonate wash solution is transferred to the 1st Cycle wash change tank for subsequent jetting to a decanter from which the aqueous phase is sent via the spent solvent aqueous hold tank to the low-activity waste hold tank. Carbon dioxide is evolved in the low-activity waste hold tank from the reaction of sodium carbonate in the spent solvent washes and nitric acid from the 2nd Product Cycle. The carbon dioxide is vented to the warm canyon process vent header. The spent acid wash solution is removed from the 1st Cycle acid washer and sent to the waste water skimmer for subsequent disposal through the Effluent Treatment Facility or general purpose evaporator, depending on the activity level of the solution.[4]

The 2nd U Cycle spent solvent flows by gravity from the mixer settler banks and is washed with about 10,000 lb of 2.5 to 5.0 wt % sodium carbonate in a continuous washer. The wash temperature is maintained at 30 to 45 °C by circulating hot water through the washer coils. The alkaline-washed solvent is pumped outside of the H-Canyon building for continuous washing with about 15,000 lb of 0.63 wt % nitric acid and then flows to the 2nd U Cycle washed-solvent hold tank. The spent sodium carbonate wash solution is transferred to the 2nd U Cycle wash charge tank for transfer to a decanter from which the aqueous phase is sent via the spent solvent aqueous hold tank to the low activity waste hold tank.[4]

The 2nd Product Cycle spent solvent is pumped continually from a hold tank and is washed with about 10,000 lb of 2.5 to 5.0 wt % carbonate in a continuous washer. Since the 2nd Product Cycle washer is not equipped to heat the wash solution, the wash temperature may vary from 30 to 45 °C depending on the temperature of the spent solvent. The alkaline-washed solvent is pumped outside the H-Canyon building for continuous washing with about 15,000 lb of 0.63 wt % nitric acid and then flows to the 2nd Product Cycle washed-solvent hold tank. If the 2nd Product Cycle wash solutions contain recoverable neptunium, they are boiled and recycled through the solvent extraction process. If not, they are disposed of in the same manner as the 2nd U Cycle wash solutions.[4]

Washing of the spent solvent with sodium hydroxide would be more effective than washing with sodium carbonate, but the use of sodium hydroxide would increase the nuclear safety hazard (see Section 2.4 on process safety). Batch washing is also superior to continuous washing; however, batch washing does not provide the capacity required for the process.[4]

2.4 Process Safety

2.4.1 Ignition of Solvent

Potential process safety issues associated with the solvent recovery process for the H-Canyon solvent extraction cycles include the possibilities of ignition of the solvent, exposure of personnel to radiation, and nuclear safety. The process solvent is flammable due primarily to the volatility of the hydrocarbon diluent. Selected properties of the H-Canyon solvent inventories (including flash points) are provided in Table 2-1. The lower explosive limit for vapor and air for dry diluent is obtained at 70 to 75 °C; this lower explosive limit is also valid for solvent containing up to 7.5% TBP. The lower explosive limit for 30% TBP – 70% diluent is 75 to 80 °C. Serious hazards in the H-Canyon facility are avoided by minimizing spillage in working areas and by keeping the solvent below its flash point at all times.[4]

Table 2-1. Properties of H-Canyon Process Solvent

Property	Value	Units
Flash point of diluent	84	°C
Flash point of 30 vol % TBP – 70 vol % diluent	89	°C
Density of 7.5 vol % TBP – 92.5 vol % diluent at 25 °C	0.774	g/mL
Density of 30 vol % TBP – 70 vol % diluent at 25 °C	0.821	g/mL
Interfacial Tension of 7.5 vol % TBP – 92.5 vol % diluent at 25 °C	13.0	dynes/cm
Interfacial Tension of 30 vol % TBP – 70 vol % diluent at 25 °C	10.0	dynes/cm
Solubility of TBP in water at 20 °C – 7.5 vol % TBP – 92.5 vol % diluent	0.18	g/L
Solubility of TBP in water at 20 °C – 30 vol % TBP – 70 vol % diluent	0.32	g/L

2.4.2 Radiation Exposure

While exposure of personnel to excessive amounts of radiation was largely eliminated by the design of the H-Canyon building, special consideration must be given to the solvent filters, the storage tanks for washed solvent, and the lines for transferring solvent between the H-Canyon building and the outside facilities. The filters accumulate radioactive solids, particularly from the alkaline solvent, and require shielding to limit radiation exposure. The storage tanks for the 1st Cycle solvent are also shielded. The solvent piping lines between the canyon building and the outside facilities are unshielded and require close surveillance during solvent extraction upsets when radiation levels as high as 400 mrem/hr were observed. The solvent tanks for the 2nd U and 2nd Product Cycles are not shielded.[4]

2.4.3 Nuclear Safety

Accumulation of a critical amount of HEU in the 1st Cycle or 2nd U Cycle continuous washers through operational errors or unforeseen process conditions should be considered, although such an accumulation is very unlikely. In the event of a total loss of uranium to the solvent washers, the maximum uranium loading of 280 g of uranium per square foot could be reached in 9.2 hours in the 1st Cycle solvent washer, and 5.9 hours in the 2nd U Cycle solvent washer. Such an event is very unlikely because the normal uranium content of the spent solvent stream from the 1st Cycle and the 2nd U Cycle is extremely low. Stripping of uranium into the aqueous product streams is so highly favored that only greatly reduced flow rates of the dilute nitric acid used to strip the uranium from the solvent could cause a significant increase in uranium concentration in the spent solvent streams. Close observations of the main solvent extraction streams by neutron monitors and continuous direct colorimetric analysis for uranium ensure that no major undetected losses to the waste streams will occur. A uranium loss of greater than 20% would quickly be detected by the colorimeters used to monitor the 1st Cycle and 2nd U Cycle product streams. A sustained uranium loss of 20% would require 1.9 days to reach the maximum uranium loading in the 1st Cycle washer and 1.2 days in the 2nd U Cycle washer. The aqueous wash solutions are also routinely sampled to prevent any undetected accumulation of uranium in the washers.[4]

Use of sodium carbonate as an alkaline wash solution reduces the criticality hazard below that which would be faced if sodium hydroxide were used. Carbonate forms a soluble complex with uranium, while sodium hydroxide precipitates sodium diuranate. Uranium is soluble to 60 g/L in 2.5 wt % sodium carbonate, whereas uranium is only soluble to about 0.05 g/L in 0.8 wt % sodium hydroxide. A welded blank in the sodium hydroxide line in the cold feed preparation area prevents the addition of caustic to the solvent recovery system. Scheduled, routine dumping of the wash solutions also eliminates the potential for a small but prolonged buildup of uranium in the solvent washers.[4]

Segregation of the various solvent systems is necessary due to the differences in the TBP concentrations. The 1st Cycle solvent and the 2nd U Cycle solvent are 7.5 vol % TBP, and the 2nd Product Cycle solvent is 30 vol % TBP. Substitution of solvent at a different TBP concentration from that used to determine the operating parameters for the mixer-settlers may in some cases lead to the refluxing and accumulation of uranium in the mixer-settlers which is a criticality issue. To prevent this, each solvent extraction cycle has a separate solvent recovery system. Since both the 2nd U Cycle washer and the 2nd Product Cycle washer use the same wash charge tank for disposing of spent wash solutions, any solvent accumulated in the wash change tank is returned to the 2nd Product Cycle solvent system rather than to the 2nd U Cycle system.[4]

2.5 Equipment

2.5.1 Continuous Washers

The equipment in the H-Canyon solvent recovery system includes facilities for collecting, adjusting, washing, decanting, and storing solvent before return to the solvent extraction process. The 1st Cycle solvent recovery system consists of two continuous washers connected in series for alkaline washing and a continuous washer outside the H-Canyon building for acid washing. The design of the continuous solvent washer is shown in Figure 2-1. The solvent washer consists of a standard 10-ft (diameter) x 11-ft (tall) tank with the conventional agitator replaced by a paddle shrouded in a 30-in pipe at the center axis of the tank. Spent 1st Cycle solvent enters the tank continuously, mixes with the wash solution, separates, and overflows into a solvent collection blister from which it is removed by pump or steam jet. The washed solvent is usually pumped to the outside acid wash tanks to avoid diluting and heating the solvent by jet condensate. Rotation of the paddle at 100 rpm provides sufficient pumping capacity to allow considerable recirculation of organic and aqueous phases within the washer. Orifice plates above and below the paddle control the relative rates of recirculation of the two phases. As designed, these orifices provide a minimum mixing ratio of about ten volumes of aqueous phase to one of organic phase. The continuous washer for acid washing of the treated solvent is essentially of the same design as the alkaline washers, except the washers are 10-ft (diameter) x 13-ft (tall) tanks, and the collection blister has been eliminated so that the solvent overflows directly to the solvent storage tanks.[4]

The 2nd U Cycle and 2nd Product Cycle solvent recovery systems include continuous washers for alkaline washing in the canyon and acid washing in the outside facilities. The unit for alkaline washing is basically of the same design as the 1st Cycle continuous washers, except the washers are 8-ft (diameter) x 11-ft (tall) tanks. These washers were designed to allow reuse of 8 to 10 wt % sodium carbonate solution for about 100-volume contacts and to produce washed solvent containing less than 0.04 wt % entrained aqueous phase. Figure 2-2 shows typical entrainment values at various mixing ratios of solvent and carbonate wash. Plant experience has indicated that the actual useful life of 2.5 wt % carbonate wash solution is about 100-volume throughputs of solvent. The units for washing the 2nd U Cycle and 2nd Product Cycle treated solvent with acid are identical to the 1st Cycle acid washer.[4]

2.5.2 Batch Washing Systems

Two systems for the batch washing of solvent are also provided in the H-Canyon facility. Each of the two batch washing systems consists of a wash tank for alkaline washing of the solvent, a decanter, a common hold tank for spent wash solutions, and a washer outside the H-Canyon building for acid or process water washing (described previously). Continuous washing of the spent solvent is performed on a routine basis. Batch washing is available as an alternate. Each wash tank is provided with a decanter which serves only that tank. A decanter is a rectangular box (7-ft (long) x 18-in. (wide) x 18 in. (deep)) that contains three sections arranged to permit organic and aqueous phases to be automatically separated by differences in density. The decanters rest on elevated frames to allow gravity discharge to the hold tanks. Figure 2-3 illustrates the flow of aqueous and organic solutions through the unit.[4]

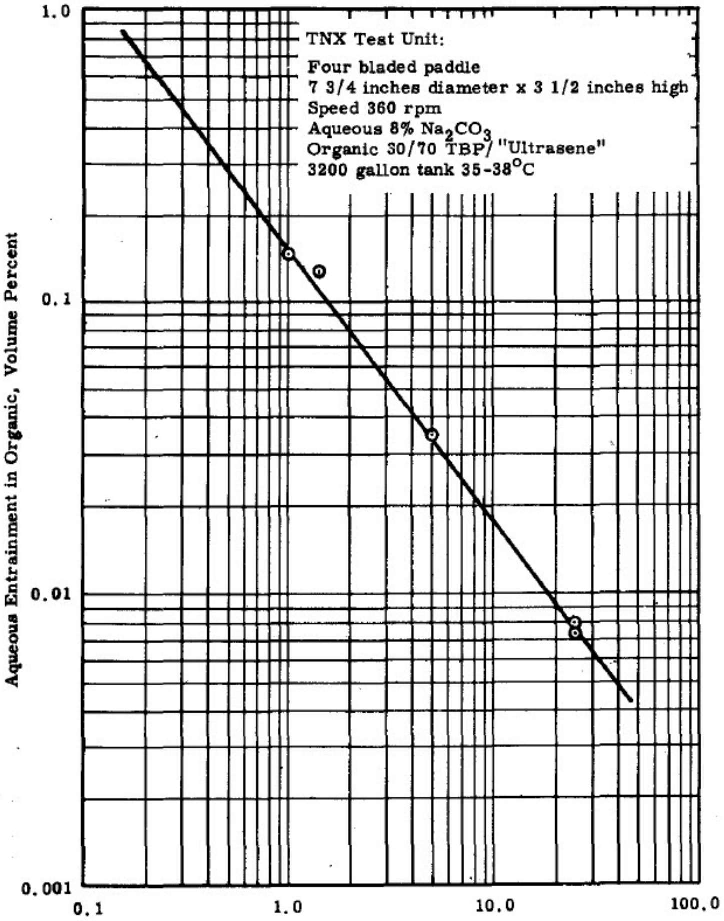

Figure 2-2. Aqueous Entrainment in Continuous Solvent Washer

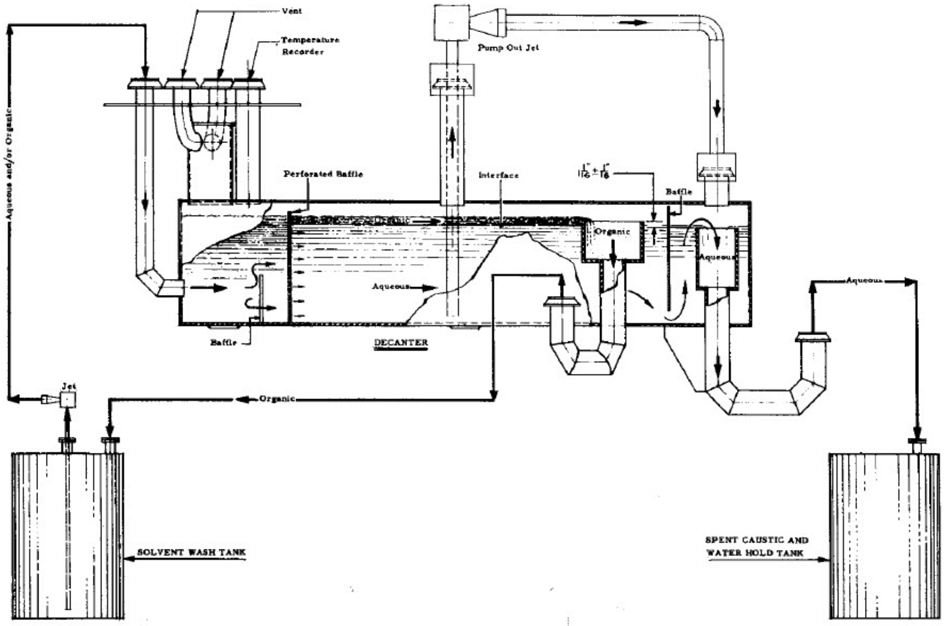

Figure 2-3. Solvent Recovery Decanter for Batch Washing

2.5.3 Pumps

The transfer of solution in the H-Canyon facility are made by steam jets or centrifugal pumps. The use of pumps for transfers is necessary where dilution of the solution by steam is unacceptable, where heating the solution is undesirable, or where a wide range of flow rates is required. The pumps used are of centrifugal, single-stage, submerged type with the shaft common to both pump and motor. The motor and bearings are located on the top of the tank. No packing or bearings are exposed to process solution. A typical pump of this type is shown in Figure 2-4.[4]

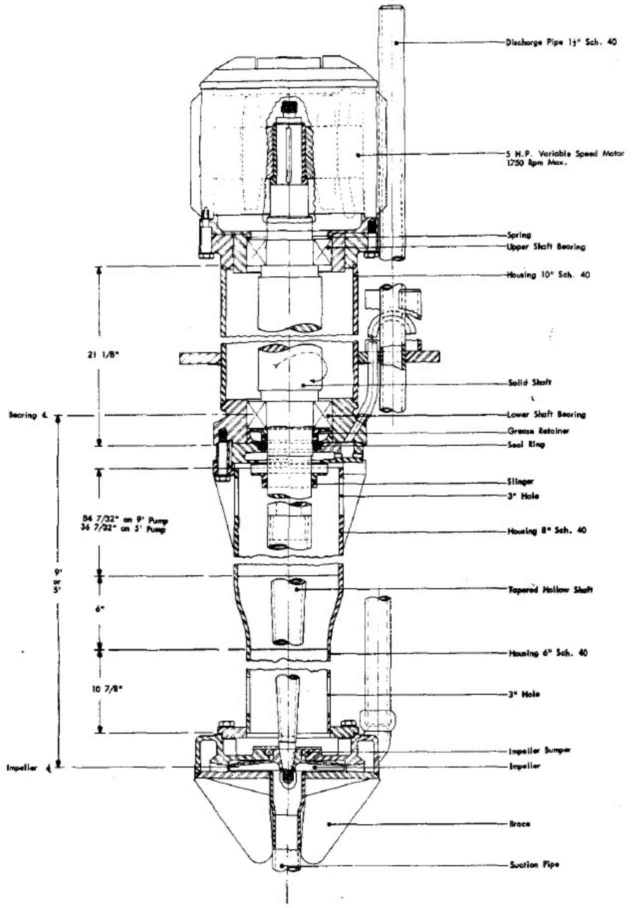

Figure 2-4. Typical H-Canyon Centrifugal Pump

Short-shaft (i.e., 5 ft) centrifugal pumps (Figure 2-4) are used to transfer the solvent from the 1st Cycle spent solvent run tank to the (1st Cycle) first continuous washer, from the first continuous washer to the second washer, from the second washer to the 1st Cycle acid washer, from the 2nd U Cycle continuous washer to the 2nd U Cycle acid washer, from the 2nd Product Cycle run tank to the 2nd Product Cycle continuous washer, and from the continuous washer to the 2nd Product Cycle acid washer. These pumps maintain adequate capacity for continuous operation. No extensive maintenance problems have been encountered with continuous pump operation.[4]

2.5.4 Storage Tanks

The alkaline washed solvents from the H-Canyon solvent extraction cycles flow by gravity from the acid washers to 10-ft (diameter) x 13-ft (tall) storage tanks in the outside facilities. From these tanks, solvent is pumped through removable filters to head tanks on the third-level of the H-Canyon facility for return to the mixer-settler banks. The filters and 1st Cycle solvent storage tanks are provided with shielded enclosures, but the radiation level of the 2nd U and 2nd Product solvent storage tanks do not require such protection. A sketch of a shielded solvent filter is shown in Figure 2-5.[4]

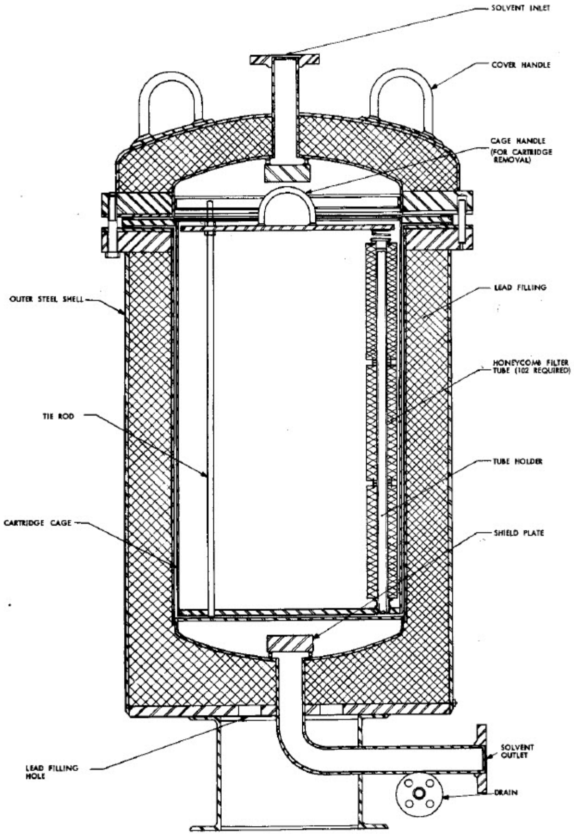

Figure 2-5. Shielded Solvent Filter

2.6 Monitoring and Analysis of Solvent Quality

In previous work at the Savannah River Laboratory, Reif and Gray recommended three criteria for use in evaluating the quality of solvent used in the three cycles of solvent extraction which operated in the SRS F-Canyon facility.[10] These criteria were also applicable to the solvent inventories used in the H-Canyon facility. The measures of solvent quality included the DBP concentration, interfacial tension, and plutonium pickup. The recommended limits for each measurement are shown in Table 2-2.

Table 2-2. Solvent Quality Limits for SRS Canyon Facilities

Measurement	Limit
DBP Content	< 30 ppm
Interfacial Tension	> 3 dyne/cm
Plutonium Pickup	< 10^4 dpm/mL alpha

Dibutyl phosphate and interfacial tension measurements were performed to measure the efficiency of the solvent washing process which SRNL demonstrated for the modified PUREX process that NIOWAVE is developing for the recovery of U from Mo-99 targets.[3] Pickup tests were not performed during the demonstration of the NIOWAVE solvent washing process as neither uranium nor plutonium were used in these tests. The metrics provided in Table 2-2 represent a good baseline for solvent quality measurements. The required frequency for measuring the solvent quality will need to be established based on experience gained from operating the process. The throughput of material, fission product inventory of the feed, frequency of operation, time the solvent inventory is in storage, and upsets encountered during operation are process characteristics which will affect the rate of solvent degradation. General instructions for the solvent quality measurement techniques in Table 2-2 are briefly described in the following sections based on the previous work performed at SRNL and available reference materials.

2.6.1 DBP Content

The SRNL measured the DBP concentration of 30 vol % TBP samples from the solvent washing demonstration by nuclear magnetic resonance (NMR) spectroscopy using a standard addition method. To perform the analysis, a sample of solvent, a sample of solvent plus 10 µg/mL DBP, and a sample of solvent plus 20 µg/mL DBP were analyzed by NMR and the DBP concentration of the sample was quantified.[3]

If the DBP content of the solvent is > 30 ppm, it may indicate that the alkalinity of the carbonate solution is below an effective threshold.

2.6.2 Interfacial Tension

The interfacial tension of 30 vol % TBP samples from the solvent washing demonstration were measured by SRNL using a modified analytical method developed for determining interfacial tension between wash solutions and process solvent from SRS solvent extraction processes.[9] This modified method was previously documented and provided to NIOWAVE at their request.[3] This method was effective but resulted in a fairly high relative uncertainty due to the number of variables measured. Additionally, the method is somewhat tedious, and it would likely be more easily deployed by obtaining a tensiometer to perform these measurements. Analytical measurements for the H-Canyon solvent extraction cycles are now performed using a Krüss DVT-10 Drop Volume Tensiometer for measuring the interfacial tension between TBP solvent and sodium carbonate solutions.[11]

If the interfacial tension of the process solvent reaches an unacceptable level, two options are available. The first option is to pass the solvent through a bed of alumina, which has been used effectively to remove normal paraffin hydrocarbon (e.g., dodecane) degradation products from the H-Canyon 1st Cycle solvent inventory.[12] The alternative option is to discard the solvent and replace it with fresh material.

2.6.3 Disengagement Time

Disengagement time is the time it takes for the organic and aqueous phases to completely separate, beginning immediately after mixing. The shorter the disengagement time, the better the performance of the solvent. This test had been used to evaluate solvent quality at SRS facilities but had poor reproducibility from operator to operator due to the subjectivity involved in judging when phase separation was complete. The interfacial tension method was developed to replace the disengagement time method since interfacial tension and disengagement time are inversely related.[9-10] Interfacial tension is typically measured between the solvent and aqueous sodium carbonate while disengagement time is typically measured between the solvent and nitric acid, so the tests are not necessarily redundant. Additionally, both tests could be performed with either sodium carbonate or nitric acid. Instructions on how to perform this test were previously provided to NIOWAVE.[3] This test does not necessarily need to be performed as often as interfacial tension measurements but can be a useful tool.

2.6.4 Pickup Tests

Solvent pickup is the residual uranium or plutonium remaining in the solvent after stripping with normal process solutions. A high value indicates that the solvent contains metal complexants (i.e., degradation products) which retain the actinides in the wash solutions while a low value indicates that a high recovery of the actinides can be expected in the product streams.[10]

Both uranium and plutonium pickup tests can be performed. Uranium pickup tests would be more appropriate for the NIOWAVE solvent extraction process than plutonium. This test can be guided by the following steps:[13]

1. Dissolve uranium at the anticipated feed concentration in representative nitric acid (3 M).
2. Contact the uranium-containing feed solution with process solvent. Typically, a 1:1 volume ratio is used for contacting the organic and aqueous solutions.
3. Scrub the solvent with representative nitric acid (3 M). Multiple contacts can be performed, but the same number must be performed for consistency between tests.
4. Strip the solvent with representative nitric acid (0.01 M). Multiple contacts can be performed, but the same number must be used for consistency between tests.
5. Measure the uranium content of the aqueous solutions (e.g., gamma counting (for enriched uranium) or inductively coupled plasma-mass spectroscopy for natural or depleted uranium).
6. Compare the amount of uranium recovered to the amount in the feed.

2.6.5 pH of Wash Solutions

The pHs of the sodium carbonate and nitric acid wash solutions should be frequently measured. As the carbonate solution decreases in pH and the acid wash solution increases in pH, replacement should be considered. Process knowledge development will aide in determining specific metrics.

3.0 References

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