Waste Acid Detoxification and Reclamation: Summary of Bench-Scale Tests for FY 1986 and FY 1987

T. L. Stewart

September 1987

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**Pacific Northwest Laboratory
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WASTE ACID DETOXIFICATION AND RECLAMATION:
SUMMARY OF BENCH-SCALE TESTS
FOR FY 1986 AND FY 1987

T. L. Stewart

September 1987

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ABSTRACT

Processes to reduce the volume, quantity, and toxicity of metal-bearing waste acid are being demonstrated at Pacific Northwest Laboratory.^(a) The primary incentives for implementing these types of waste minimization processes are regulatory and economic (that is, they meet requirements in the Resource Conservation and Recovery Act and reduce the cost for treatment, storage, and disposal). Two precipitation processes and a distillation process are being developed to minimize waste from fuel fabrication operations, which comprise a series of metal-finishing operations. Waste process acids such as HF-HNO₃, etch solutions containing Zr as a major metal impurity, and HNO₃ strip solution containing Cu as a major metal impurity are detoxified and reclaimed by concurrently precipitating heavy metals and regenerating acid for recycle. Acid from a third waste acid stream generated from chemical milling operations will be reclaimed using distillation. This stream comprises HNO₃ and H₂SO₄ containing U as the major metal impurity. Distillation allows NO₃⁻ to be displaced by SO₄²⁻ in metal salts; free HNO₃ is then vaporized from the U-bearing sulfate stream. Uranium can be recovered from the sulfate stream in a downstream precipitation step. Operating conditions for each of these processes are being determined and will be used as a basis for pilot plant design.

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1.0 INTRODUCTION

The U.S. Department of Energy's Hazardous Waste Remedial Actions Program (DOE-HAZWRAP) has funded the Waste Acid Detoxification and Reclamation (WADR) project since FY 1986. The work is being conducted by staff at the Pacific Northwest Laboratory (PNL)^(a) in Richland, Washington. The objective of the project is to adapt and demonstrate a process and process equipment to reduce the volume, quantity, and toxicity of metal-bearing waste acids generated from metal-finishing operations. The goal is to detoxify the acid by removing heavy metals and radionuclides and reclaim the acid for recycle. Where economically feasible, metals or metal salts can be recovered for reuse as well. Therefore, this process will constitute a method for waste minimization. Waste acids of particular interest include nitric, hydrofluoric, hydrochloric, and sulfuric acids, because these acids are commonly used in the nuclear industry. The primary emphasis of the project is to identify, evaluate, and demonstrate methods such as precipitation and distillation with sulfuric acid to meet the stated goals.

The approach taken in this multiyear project is to:

- identify the process stream(s) to be used for demonstration
- select the detoxification and reclamation processes that could be used to regenerate the acid
- determine the operating conditions for the proposed process using bench-scale equipment
- demonstrate this process on a pilot scale.

During FY 1986 and FY 1987 the process stream was selected, a waste acid detoxification and reclamation process was proposed, and operating conditions for this process were determined. These data will be used to design a pilot plant for demonstration of the process at a metal-finishing facility in future years.

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Large bench-scale equipment was used to determine the operating conditions for the proposed process. In this report, results of these bench-scale tests will be summarized. In Section 2.0 a description of the current and proposed processes will be presented. In Sections 3.0 and 4.0, test results for the two acid detoxification processes selected for development will be discussed. Section 5.0 presents test results from an acid reclamation process. A summary will be provided in Section 6.0.

2.0 CURRENT AND PROPOSED PROCESSES

This section describes the current metal-finishing process streams selected for use in the WADR demonstration and the proposed processes for detoxification and reclamation.

2.1 DESCRIPTION OF CURRENT METAL-FINISHING PROCESS

The metal-finishing process streams selected for use in the WADR demonstration are generated during nuclear fuel fabrication. Fuel fabrication is a series of metal-finishing operations, such as chemical milling, stripping, and etching, operated in a batch mode. During operation, the concentration of one major metal impurity reaches a maximum limit, and the acid is discharged for downstream treatment as shown in Figure 2.1. At the time of discharge, the acid stream contains a high concentration of acid, a high concentration of the one major metal impurity, and very dilute concentrations of several minor metal impurities introduced from the metal alloys used in fuel fabrication.

Specifically, the chemical milling solution contains $\text{HNO}_3\text{-H}_2\text{SO}_4$, with U as the major metal impurity. The strip solution contains HNO_3 with Cu as the major metal impurity, and the etch solution contains HF-HNO_3 with Zr as the

FIGURE 2.1. Current Fuel Fabrication Process

major metal impurity. Two minor metal impurities in the strip solution, Si and U, influence the detoxification method selected. Silicon forms a gelatinous orthosilicic acid that can interfere with separation techniques. The U is a valuable material that would be worth recovering if technically feasible.

Current treatment of these waste streams includes neutralization of the U-bearing stream generated from chemical milling operations to adjust pH and remove U as a sodium diuranate. The diuranate is recovered for refining. Similarly, the Cu-bearing solution discharged from stripping operations and the Zr-bearing solution discharged from etching operations are also neutralized. The neutralized streams undergo a solid/liquid separation; the solids are sent to disposal, and the liquids are stored for future disposal.

There were several reasons for selecting the waste acid process streams from fuel fabrication for use in the WADR demonstrations:

1. The volume of the neutralized acid discharged from the process is on the order of 10^6 L/yr and will contribute to the load on double-shell tank storage space. Therefore, reduction in the volume of this waste would have a positive impact on waste management practices.
2. These wastes contain nitrates that are mobile in the environment and will require additional considerations or constraints on performance criteria for the final waste form. Therefore, it would be desirable to reduce or eliminate nitrates from the waste stream.
3. Because HNO_3 is commonly used in the nuclear industry, demonstration of a method for reducing the volume of nitrate wastes would be transferrable to or supportive of the development of similar efforts for other waste process streams at DOE facilities.
4. Fuel fabrication streams are amenable to detoxification and reclamation processes because their composition is relatively constant and the volume for each type of stream is great enough (i.e., on the order of 375,000 L/yr) to make this approach economically feasible.

2.2 PROPOSED PROCESSES FOR DETOXIFICATION AND RECLAMATION

Candidate methods for detoxification and reclamation of each waste stream were discussed in reports by Wick, Elmore, and Hartley (1983), Weakley (1984), and Stewart and Hartley (1985). These methods included precipitation, electro-winning, resin bed exchange, distillation, and membrane separation. Preliminary screening test results indicated that precipitation was the method of choice for detoxifying and reclaiming the Cu- and Zr-bearing acids. Furthermore, distillation with sulfuric acid should be selected for reclamation of the U-bearing acid and acid discharged from stripping and etching operations after rejuvenation and recycle are no longer possible (Weakley 1984). These methods were selected because of:

- technical and economic feasibility
- compatibility with disposal scenario
- compatibility with current procedures and available space in the plant
- availability of commercial equipment.

Figure 2.2 illustrates the proposed flowsheet for the fuel fabrication process that incorporates these detoxification and reclamation operations.

2.2.1 Precipitation Process for Rejuvenation of Zr-Bearing Waste Acid

Etch solutions can be reclaimed for recycle at the point of generation by removing Zr from the HF-HNO₃ solution as a zirconate salt using NaF as the precipitant. The precipitation reaction is shown in Equation (1).

The resulting filtrate is recycled to the etch operation, and the zirconate salt (sodium hexafluorozirconate) could be sold to the aluminum industry as a by-product for alloying or could be disposed of as a hazardous waste after neutralization and dewatering. Because minor metal impurities will eventually concentrate with recycle, the etch solution may have to be discharged once or twice a year to maintain quality of the acid for etching fuel rods. At the

FIGURE 2.2. Proposed Acid Recovery Process

time of such a discharge, the same precipitation reaction would be used to detoxify the waste acid before it is sent downstream for final reclamation in a distillation process (see Figure 2.2).

2.2.2 Precipitation Process for Rejuvenation of Cu-Bearing Waste Acid

Similarly, the strip solution would be reclaimed at the generation point, using precipitation with oxalic acid to remove the Cu, as shown in Equation (2). Silicon present as a gelatinous orthosilicic acid in the waste acid is physically, rather than chemically, removed during filtration.

The resulting filtrate would be recycled to the strip operation and the solids would be disposed as mixed waste. The solids are acidic and will have to be neutralized before final packaging for disposal. During this neutralization,

CuC_2O_4 is thermally degraded to CuO , a less toxic waste. It is desirable to keep the U in solution during precipitation and allow it to concentrate by recycling. Eventually, the strip solution must be discharged as the concentration of HNO_3 drops from about 13.0 M to below 3.0 M. Dilution of the acid occurs during normal stripping operations because of conversion of some HNO_3 to NO_x . The nitrate lost as NO_x cannot be regenerated in the proposed precipitation process; only nitrate in solution as $\text{Cu}(\text{NO}_3)_2$ can be regenerated. Therefore, at a specified HNO_3 concentration, the strip solution would be discharged, the Cu removed via precipitation (detoxification), and the U recovered for refining during the final downstream reclamation step using distillation.

2.2.3 Distillation Process for Reclamation of Waste Acid

In the final downstream reclamation step, NO_3^- and F^- would be recovered as acid using distillation with H_2SO_4 , then recycled to the metal-finishing operations. The stream to be reclaimed would comprise, primarily, the chemical milling solution, but would also include unrecyclable detoxified streams discharged from etching and stripping operations. The reasons for using H_2SO_4 in this step are to 1) displace NO_3^- in the metal salts, thus forming sulfate salts, and 2) allow separation of free HNO_3 and HF from these salts by distilling them to the overhead stream. Normally, at concentrations below their azeotropes, HNO_3 and HF would concentrate in the bottoms stream. In the presence of H_2SO_4 , the azeotrope is shifted and HNO_3 is concentrated in the overhead stream (Ellis and Thwaites 1957). Hydrofluoric acid may also be concentrated in the overhead stream, but this must be verified experimentally. Because H_2SO_4 is present in the chemical milling stream, little or no additional H_2SO_4 would be added to achieve this separation. Uranium in the bottoms stream can then be recovered for refining in a downstream neutralization step. The final waste stream from the reclamation process would be reduced in volume as a result of the acid separation and the final effluent would contain sulfate salts that are less mobile in the environment than the nitrate salts.

3.0 BENCH-SCALE PRECIPITATION TESTS - Zr-BEARING HF-HNO₃

The primary objective of the bench-scale precipitation tests was to determine the trends in Zr removal, cake characteristics, and solid/liquid separation characteristics as operating conditions were varied. A secondary objective was to initiate evaluation of equipment performance and to develop operating procedures applicable to pilot plant operations.

Equipment used in the bench-scale precipitation system can be divided into three major categories: reaction/crystallization, separation, and air quality control. The type and configuration of equipment chosen for the system are similar to that likely to be used for pilot-scale operation.

The bench-scale system is shown in Figure 3.1. Equipment included a 95-L agitated reaction/precipitation tank, a recessed chamber filter press with a capacity of 0.014 m³, and a scrubber for control of acid fumes. Teflon® heat exchange coils were placed in the tank to provide heating and cooling capability. Wetted surfaces in contact with heated HF-HNO₃ were constructed of polypropylene or fluoropolymers. Surfaces in contact with the acid solutions at ambient temperature were constructed of polypropylene, polyethylene, fluoropolymers, or polyvinyl chloride. Nonwetted surfaces included fiberglass (for reinforcement) and steel.

Waste acid used in these tests was actual effluent from etching operations. Acid concentrations averaged 17 g/L HF and 400 g/L HNO₃, with Zr concentration averaging 45 g/L (Weakley 1984). Because the solubility of Na₂ZrF₆ is weakly dependent on HF concentration, which varied between batches, makeup HF was added to the waste acid before reaction to a concentration of 22 g/L, the maximum concentration expected during etching operations. Minor metal impurities in solution included Al, Be, Cr, Cu, Fe, Ni, and Si, which are typically present in concentrations of <0.1 g/L.

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FIGURE 3.1. Bench-Scale Equipment for Precipitation Processes

3.1 TEST PROCEDURES

The general approach for determining the trends in Zr removal, cake characteristics, and solid/liquid separation characteristics was to establish a reference set of conditions and procedures that could be varied one at a time for comparison. The conditions to be varied included reaction temperature, stirring speed during reaction and crystallization (i.e., impeller tip speed), stoichiometry, and length of reaction and crystallization periods as listed in Table 3.1. The reference reaction conditions are listed in Table 3.2; they were established based on information available in the literature (Megy and Propst 1978).

TABLE 3.1. Tests Conducted for Zr Precipitation Process

Run No.	Reaction Temperature, °C	Reaction/Mixing Impeller Tip Speed, cm/sec	Stir Time, min	Method of NaF Addition	Stoichiometric Addition, g NaF/g Zr	Cryst. Time, h	Cryst. Impeller Tip Speed, cm/sec
1(a)	Heatup	30,320,570	--	--	--	--	--
2	20	320	15	Solid	0.83	4	0
3	40	320	15	Solid	0.83	4	0
4	60	320	15	Solid	0.83	4	0
5(b)	40	570	15	Solid	0.83	4	0
6	40	30	15	Solid	0.83	4	0
7	40	320	60	Solid	0.83	4	0
8(c)	40	320	15	Slurry	0.83	4	0
9	40	320	15	Solid	0.55	4	0
10	40	320	15	Solid	1.15	4	0
11	40	320	15	Solid	0.83	8	0
12	40	320	15	Solid	0.83	24	0
13	40	320	15	Solid	0.83	4	570
14	40	320	15	Solid	0.83	4	30
15	40	320	15	Solid	0.83	4	320

- (a) Effect of impeller tip speed on heat transfer properties was determined. No reaction occurred.
 (b) Maximum impeller tip speed obtainable with this system. It also corresponds to the scaled-down tip speed used in a commercial process.
 (c) Planned but not conducted.

TABLE 3.2. Reference Conditions for HF-HNO₃
Rejuvenation Tests

Reaction Temperature	40°C
Impeller Tip Speed	320 cm/sec
Stoichiometry	0.83 g NaF/g Zr
Reaction Time	15 min
Crystallization Time	4 h
NaF Addition	Solid

Data collected for each run included acid analysis with inductively coupled plasma (ICP) to determine cation concentration and titration to determine H⁺ concentration, filtering characteristics, and cake characteristics. Filtering characteristics included solid and filtrate yield rates as well as back pressures during filling cycle. Cake characteristics included moisture content and composition. Selected solid samples were analyzed with scanning electron microscopy (SEM) to determine changes in particle shape and size with changing process conditions and with X-ray diffraction (XRD) to determine the solids composition.

3.2 RESULTS OF Zr PRECIPITATION TESTS

Test results indicated that acceptable Zr removal could be achieved at 90% stoichiometry (i.e., 0.83 g NaF/g Zr) for any operating condition that ensures adequate dispersal of solid NaF during reaction. Acceptable Zr removal was defined in terms of final acid composition. Final Zr concentration of less than 7 g/L and final Na concentration of 1 g/L or less were set as limits, based on data reported by Megy and Propst 1978. Zirconium removal averaged 85% (i.e., final Zr concentration averaged 5.8 g/L with Na concentrations averaging 1 g/L) except at low impeller tip speeds during solid dispersal and reaction, when it dropped to 40%. Under these conditions, solid NaF was not readily dispersed and dissolved as it was added to the waste acid. Reaction may have been localized on the solid surfaces, coating the crystal and inhibiting dissolution.

As can be seen in Figure 3.2, HF concentration nearly doubled and HNO_3 concentration appeared to decrease by 14% as Zr was removed. Megy and Propst (1978), Sattler (1981), and Fenneman (1981) reported that the reaction was

However, mass balances based on these test results did not agree with this reaction statement. Solution analysis of the discharged etch solution in which total F^- and total NO_3^- were measured indicated that Zr^{4+} complexed with six F^- and existed as H_2ZrF_6 in solution. Hence, the actual reaction was that shown in Equation (1), which accounts for an increase in HF concentration. The apparent decrease in HNO_3 concentration is caused by the analytical technique used. The concentration of HNO_3 in the waste acid was assumed to be the difference in the concentration of total acid and HF measured by titration. This technique did not account for the presence of H_2ZrF_6 separate from the HNO_3 . In pilot plant operations, a combination of NaF/NaNO_3 precipitants or dilution

FIGURE 3.2. Composition of HF- HNO_3 Etch Solution Before and After Reclamation Using Zr Precipitation

of reclaimed etch solution with acidic cake wash water may be required to generate a rejuvenated etch solution that will meet tank make-up specifications upon recycle.

Test results also indicated that reaction temperature and stoichiometry affected particle size and shape, which, in turn, determined the type of filtration equipment required to produce acceptable solid/liquid separation. (For this application, acceptable solid/liquid separation includes both clear filtrate with <1 vol% solids and dewatered solids that release no freestanding liquid after packaging.) Figures 3.3 and 3.4 show particle characteristics. The average particle diameters for cakes formed at different operating conditions ranged from 3 to 20 μm by population; 3- μm particles were individual platelets, and 15- to 20- μm particles were agglomerated platelets that appeared as rosette shapes. Agglomeration was observed for reactions at 20 and 60°C. Agglomeration was not observed at 40°C, regardless of stoichiometry, although particle size did increase by a factor of 10 for reaction at 125% stoichiometry as compared with those at 60% stoichiometry (see Figure 3.4).

In addition, reaction temperature and stoichiometry affected cake composition. Under those conditions in which Na was available at a rate less than the reaction rate to produce Na_2ZrF_6 , a second zirconate salt, $\text{Na}_7\text{Zr}_6\text{F}_{31}$, formed. These conditions occurred at a reaction temperature of 20°C and stoichiometry of 60%. The $\text{Na}_7\text{Zr}_6\text{F}_{31}$ salt is believed to hydrate, forming a wetter cake that may liberate freestanding liquid when the cake is placed in a drum. Freestanding liquid must be avoided if the cake is disposed of as a hazardous waste. Therefore, it is preferable to choose those reaction conditions that produce Na_2ZrF_6 .

Based on results of these tests, operating conditions for the Zr precipitation to be used as the reference procedure in the pilot plant include reaction temperature of 60°C, impeller tip speeds of 320 cm/sec during solid dispersal/reaction using a moderate shear impeller such as the Lightnin A310®, addition of 0.83 g NaF/g Zr in solution, and 24-h crystallization periods. The choice of reaction temperature is based primarily on the measured particle size

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20 μm

20°C, 90% Stoichiometry

20 μm

60°C, 90% Stoichiometry

20 μm

40°C, 90% Stoichiometry

FIGURE 3.3. Particles Formed at Various Reaction Temperatures

20 μm

40°C, 60% Stoichiometry

20 μm

40°C, 125% Stoichiometry

20 μm

40°C, 90% Stoichiometry

FIGURE 3.4. Particles Formed at Various Stoichiometric Additions of NaF

and formation of the Na_2ZrF_6 salt. An optional reaction temperature of 20°C should be considered, however, for further investigation in the pilot plant. The reasons for this recommendation center on the following observations:

- Particle agglomeration also occurred at this temperature.
- Reaction at the lower temperature would have several benefits, including longer equipment life, fewer acid fumes, and improved operator safety.
- The number of duplicate runs were limited in these tests, requiring that trends be confirmed during pilot operations.

The choice of impeller tip speed is based on the measured decrease in Zr removal at lower tip speeds, apparently because of poor solids dispersal and dissolution. Addition of NaF at a mass ratio of 0.83 g NaF/g Zr (90% stoichiometry) was chosen to ensure availability of Na at a rate equal to the reaction rate to form Na_2ZrF_6 and subsequently avoid formation of the wetter $\text{Na}_7\text{Zr}_6\text{F}_{31}$ cake. Furthermore, 90% stoichiometry allows for an excess of Zr in the recycle stream to reduce the potential for precipitation on the surface of the fuel rods during etching. Finally, a crystallization period of 24 h was chosen to accommodate normal work shifts.

Engineering considerations based on test results include the following:

- A filter press will provide acceptable solid/liquid separation even during process upsets without use of a precoat. The diaphragm pump functioned well during these tests and is recommended for the pilot operation.
- Construction materials showed no obvious degradation during bench-scale tests suggesting that catastrophic failure would not be expected.
- A heat-exchange system that can provide both heating and cooling will be needed. It should be sized for the cooling operation rather than the heating because the temperature-driving force, ΔT , is lower for

cooling than for heating and because adequate cooling will reduce the chance for delayed precipitation that could cause pluggage in pipes, pumps, and storage tanks.

Solid/liquid separation characteristics were determined, including solid and filtrate yield rates, fractions of solids in reaction slurry, discharge pressure from the diaphragm pump used to fill the press, filter cake moisture content, and bulk density of the cake. Averages of the results for all tests are listed in Table 3.3. These data will be used during engineering scale-up in FY 1987 and in economic analyses. The solid-yield rates could be categorized as slow, requiring pressure as a driving force for separation. On the other hand, the liquid-yield rates indicate a medium filtration rate, requiring only a vacuum. Use of a filter press for separation will accommodate both these separation characteristics.

TABLE 3.3. Solid/Liquid Separation Characteristics for HF-HNO₃ and Zirconate Salt Slurry

Characteristic	Average Value	Range
Solid yield rate, kg dry solid/m ² ·h	120	50-220
Filtrate yield rate, L/m ² ·h	1050	530-1530
Fraction of total solids in slurry, wt%	6	3-8
Discharge pressure, psig	22	4-34
Cake moisture content, wet wt%	50	26-64
Bulk density of wet filter cake, g/cm ³	1.9	1.6-2.4

4.0 BENCH-SCALE PRECIPITATION TESTS - Cu-BEARING HNO₃

The primary objective of this activity was to determine the trends in selective Cu and silicic acid removal from waste stripping solution while regenerating HNO₃ as operating conditions were varied. In addition, cake and solid/liquid separation characteristics were to be determined under various operating conditions. A secondary objective was to initiate evaluation of equipment performance and to develop operating procedures for the pilot plant.

The bench-scale system shown in Figure 3.1 was modified for Cu precipitation tests. Specifically, a second reaction/precipitation tank was added for storage and heating of a seed slurry, and the scrubber system was upgraded to handle an anticipated increase in NO_x release. Seed slurry comprised HNO₃ and CuC₂O₄ formed during previous reactions. The seed slurry was added to the reaction solution to try to enhance particle growth rates.

Waste acid used in these tests was actual effluent from the fuel fabrication stripping operations. Under current fuel fabrication operations, the acid composition at discharge averages 4.8 M HNO₃, 180 g/L Cu, and 3.3 g/L U (Weakley 1984). For these tests, the initial Cu concentration was reduced to 100 g/L and 150 g/L by adding 57 wt% HNO₃ as needed; concentrations vary with each batch. The dilution was equivalent to discharging the waste acid from the stripping process more frequently during actual operations. Dilution was used because Cu removal was expected to improve with reduced initial Cu concentration (Stewart and Hartley 1985). Cu removal at lower initial Cu concentrations is improved by the reduced concentration of silicic acid; Si is an alloy in the Cu cladding being stripped and, hence, Si concentration is proportional to Cu concentration. The gelatinous silicic acid tended to coat the solid oxalic acid particles and inhibit the rate of dissolution of the crystals at higher Cu/Si concentrations.

4.1 TEST PROCEDURES

The general approach for determining the trends in Cu and Si removal, cake characteristics, and solid/liquid separation characteristics was to select ranges for reaction temperature, initial Cu concentration, and length of

reaction and crystallization periods and then to vary each of these conditions for comparison. Also, seed solution was used in some tests to determine if addition of seed solution improved particle growth rate. The conditions evaluated are listed in Table 4.1.

Data collected for each run included acid analysis using ICP to determine cation concentration and titration to determine H^+ concentration, filtering characteristics, and cake characteristics. Filtering characteristics included solid and liquid yield rates as well as back pressure during the filling cycle. Cake characteristics included moisture content and particle size. Selected samples of the cake were analyzed using the SEM to determine average particle size and shape.

4.2 RESULTS OF Cu-PRECIPITATION TESTS

Test results indicated that similar Cu removal was achieved at 90 to 100% stoichiometry for all operating conditions tested. For initial Cu concentrations of 100 g/L or 150 g/L Cu, an average of $88 \pm 20\%$ Cu was removed with an average of $73 \pm 24\%$ HNO_3 regenerated (see Figure 4.1). These results suggest that dilution of the Cu strip solution was not necessary to attain acceptable Cu removal.

Cake characteristics such as particle size and shape did not appear to be significantly affected by reaction temperature, use of a seed solution, or length of a crystallization period, as can be seen in Figure 4.2. The irregularly shaped particles averaged $0.5 \mu m$ in size by population, ranging from 0.1 to $2.1 \mu m$. Because of the small particle size, a precoat was used in the filter press to improve solid/liquid separation. Although use of precoat reduced the fraction of solids in the filtrate, the volume fraction of solids exceeded 1%. Pump discharge pressure averaged 74 psig because of the increased capillary pressure associated with small particles; this pressure was near the operating limits of the bench-scale system. The filter cake released readily from the filter media, but had a gel-like consistency from the presence of silicic acid. Freestanding liquid was not observed in the cake packaged in disposal containers. Based on these results, acceptable solid/liquid separation that included both filtrate with $<1 \text{ vol}\%$ solids and dewatered solids that

TABLE 4.1. Tests Conducted for Cu-Precipitation Process

Run No.	Cu Conc., g/L	Reaction Temp., °C	Reaction Time, min	Crystal. Time, h	Seed Used
1	150	20	60	24	yes
2	150	60	60	24	no
3	150	60	15	4	no
4	150	20	60	4	yes
5	100	60	15	4	no
6	100	60	15	24	no
7	100	90	60	24	no
8	100	90	60	24	yes
9	100	118 ^(a)	60	24	yes
10	100	20	60	24	yes
11	100	20	60	24	no

(a) Normal boiling point.

do not release freestanding liquid after packaging was partially, but not completely, achieved. Solid/liquid separation characteristics are listed in Table 4.2. Both solid and liquid yield rates were slow. Therefore, it is recommended that either a pressure filtration system or an improved filter press system be considered for pilot-plant operations.

FIGURE 4.1. Composition of HNO_3 Strip Solution Before and After Reclamation Using Cu Precipitation

(a)

(b)

FIGURE 4.2. Particles of CuC_2O_4 Formed at (a) 60°C With a 24-h Crystallization Period and No Seed Solution and (b) 20°C with a 4-h Crystallization Period and Seed Solution Added at 1:1 Volume Ratio

TABLE 4.2. Solid/Liquid Separation Characteristics for HNO_3 and CuC_2O_4 Slurry

Characteristic	Average Value	Range
Solid yield rate, $\text{kg dry solid/m}^2\cdot\text{h}$	85	40-120
Filtrate yield rate, $\text{L/m}^2\cdot\text{h}$	290	140-460
Fraction of total solids in slurry, wt%	16	10-24
Discharge pressure, psig	74	60-80
Cake moisture content, wet wt%	35	26-43
Bulk density of wet filter cake, g/cm^3	1.2	0.8-1.7

Based on test results, recommended reference operating conditions for Cu precipitation include a reaction temperature of 60°C, initial Cu concentration of 150-180 g/L, and a crystallization period of 24 h. Seed solution will not be necessary. Test results indicated that reaction temperature had no effect on Cu removal or efficiency of acid regeneration for solutions containing 100- or 150-g/L Cu initially. Lower reaction temperatures have benefits such as increased equipment life, lower concentration of acidic fumes released, and operator safety. These lower temperatures should be investigated on the pilot scale to verify bench-scale observations.

Tests also indicate that Cu removal and acid regeneration were not affected by the initial Cu concentration, suggesting that more frequent discharge of the waste acid (hence, lower initial Cu concentrations) would not be necessary. Therefore, acid from fuel fabrication stripping operations will be sent to the detoxification step (i.e., precipitation) as Cu concentration in the strip solution approaches 150 to 180 g/L. A crystallization period of 24 h was chosen to accommodate normal shifts. Finally, use of seed slurry did not appear to improve the rate of particle growth; therefore, it will not be used in pilot plant operations.

Engineering considerations based on the test results include the following:

- A pressure filtration system or improved filter-press system will be required to achieve acceptable solid/liquid separation. Specifically, filtrate clarity must be improved by reducing total solids to <1 vol%. Filter media with a smaller particle retention size or use of precoat or body feed may improve clarity. Adequate pump pressure and volumetric flow rate must be provided.
- Construction materials for the bench-scale system were adequate, showing no sign of catastrophic failure during the tests. Therefore, polypropylene or fluorocarbons are recommended for the pilot plant.
- A NO_x scrubber system will be required.

5.0 BENCH-SCALE DISTILLATION TESTS - U-BEARING $\text{HNO}_3\text{-H}_2\text{SO}_4$

The primary objectives of the distillation tests were to determine the rate and type of corrosion or degradation of candidate materials of construction for the wetted surfaces of the distillation system to be used for final acid reclamation and to determine specific equilibrium data unavailable in the literature by conducting distillation tests. Additional objectives were to evaluate the performance of a large bench-scale column and to initiate development of operating procedures for the pilot plant.

The bench-scale system shown in Figures 5.1 and 5.2 was used for some of the corrosion tests and to determine column performance. In the future this system will also be used for distillation tests. The column, reboiler, and condenser system is constructed of fiberglass-reinforced ethylene-chlorotrifluorethylene (E-CTFE). The reboiler capacity is 40 L. The column has a diameter of 10.3 cm and is filled with 1.6-cm Pall rings constructed of E-CTFE for a packing to column diameter ratio of 1:6.4. The heat exchangers in both the reboiler and the condenser are reactor coils consisting of spaghetti tube bundles constructed of tetrafluorethylene-hexafluoropropylene (FEP) with a surface area of 2.3 m^2 . A polyvinylidene fluoride (PVDF) jet eductor is used to maintain a vacuum of 300 mm Hg absolute on the system during operation. Steam to the reboiler is provided by a packaged steam generator system. The vacuum regulation system, shown in Figure 5.3, is placed downstream of the condenser to scrub the offgas and control the vacuum in the system. The column is fully instrumented with thermocouples and pressure gauges. A micrologger is used to both control the system and record data collected during operation.

In addition to this bench-scale unit, smaller laboratory-scale vessels and distillation systems were used for both distillation and corrosion tests. These systems included a 650-mL round bottom flask, a Liebig condenser, and a 200-mL receiving flask constructed of Teflon.®

®Product of DuPont de Nemours, Wilmington, Delaware.

FIGURE 5.1. Large Bench-Scale Distillation System for Acid Reclamation

FIGURE 5.2. Diagram of Large Bench-Scale Distillation System for Acid Reclamation

FIGURE 5.3. Vacuum Regulation System for Distillation Process

5.1 PROCEDURE FOR CORROSION TESTS

Wetted surfaces of the distillation system will contact HF, HNO₃, and H₂SO₄ in concentrations ranging from 0 to 10% HF, 0 to 30% HNO₃, and 0 to 80% H₂SO₄. The temperature of these acid mixtures will range from 25 to 100°C. Although chemical resistance data can be found for the candidate materials of construction exposed to the individual acids, very little information is available for the ternary acid mixture. Therefore, additional corrosion or degradation data were required for design of the pilot plant equipment. Specifically, the type of corrosion such as pitting, granulation, or embrittlement coupled with data on the rate of this corrosion would provide a basis for selecting thickness of coatings for the system components. Of particular interests was the thickness of thermoplastic coating required for the heat exchange equipment.

The approach taken to determine the rate and type of corrosion was to conduct both static and dynamic tests. Static tests were defined as those tests in which test coupons of candidate thermoplastics would be exposed to various acid compositions and temperatures in stirred vessels. Dynamic tests were defined as those tests in which the coupons were placed in the large bench-scale column and exposed to simulated operating conditions. The coupons for both tests were to be exposed to the various conditions for 1, 10, and 100 days nominal. At the end of the designated periods, the weight, thickness, and hardness were measured to determine the type and rate of physical and mechanical changes in the materials. The hardness was measured with a Type D Durometer instrument. In addition, visual observation were made to record changes in color or form. Based on these test results, the modulus of elasticity was determined for selected coupons.

The acid compositions used in the static tests reflected various average annual acid compositions likely to be encountered in the actual distillation system. These are listed in Table 5.1. The composition labeled Case I reflects the average annual composition of the chemical milling solution: the primary feedstream to the distillation (i.e., reclamation) process. The

TABLE 5.1. Composition of Acid Used in Corrosion Tests to Simulate Actual Waste Acid

Case Number	Composition, wt%			
	HF	HNO ₃	H ₂ SO ₄	H ₂ O
I(a)	--	19	32	49
II(a)	0.1	21	28	50.9
III(a)	--	11	60	29
IV(a)	0.06	11.67	60	28.27
V(b)	--	57	--	43
VI(b)	0.2	57	--	42.8

(a) Possible composition of acid feed to evaporator.

(b) Possible composition of acid in overhead vapor product stream.

Case II stream is the reference composition and reflects the composition of the chemical milling solution plus the detoxified streams from the stripping and etching operations. The volume of the detoxified streams based on the results of the bench-scale precipitation test is estimated to be 10 vol% of the currently generated stripping solution and 2 vol% of the currently generated etching solution. Based on equilibrium data found in the literature for the HNO_3 - H_2SO_4 - H_2O system, 100% of the HNO_3 can be recovered at a concentration of 57 wt%, the concentration used for fresh makeup acid in the current fuel fabrication operations, if the composition of the feedstream is 60 wt% H_2SO_4 initially. Therefore, the composition of acids for Cases III and IV are the same as Cases I and II, respectively with the concentration of H_2SO_4 increased to 60 wt%. Cases V and VI reflect possible vapor compositions found in the column; in Case V, the initial feedstream would have been the chemical milling solution alone, and in Case VI, the initial feedstream would have been the reference stream.

A set of candidate materials of construction included: polychlorotrifluoroethylene (PTFE), tetrafluoroethylene (TFE), FEP, E-CTFE, PVDF, polypropylene, and polyvinyl chloride (PVC). Sets of these coupons were suspended in six stirred vessels filled with acid for tests conducted at ambient temperatures. Acid solutions used in these tests were those listed as Cases I through VI in Table 5.1. One set of coupons was placed in a round-bottomed flask containing acid with the reference composition (i.e., Case II in Table 5.1) and maintained at a temperature of at 100°C . Four sets of coupons were placed in the large bench-scale system for the dynamic corrosion tests: two sets in the reboiler, one set in the vapor above the reboiler liquid, and one set in the packing at the top of the distillation column. The feed solution for the large bench-scale tests was that described by Case II in Table 5.1 (i.e., reference condition). The temperatures in the column ranged from 85°C in the reboiler liquid to 80°C in the vapor above the reboiler liquid to 70°C in the vapor at the top of the column.

5.2 CORROSION TEST TRENDS

Corrosion tests will be conducted for a minimum of 100 days during FY 1987; at the time this report was prepared, data for the static tests after 76 days of exposure were available.

At ambient temperatures, the effects of various acid compositions on each of the seven candidate materials were observed in static tests. After 76 days of exposure, trends indicate that all candidate materials such as transfer pipes and storage tank liners would be suitable for service at ambient temperatures for the combinations of $\text{HF-HNO}_3\text{-H}_2\text{SO}_4$ likely to be encountered within the reclamation system. There were no measurable changes in weight for any of the samples except the FEP sample for which a change of 2 to 4 wt% was measured over the various acid conditions. However, this weight change was attributed to the dissolution of fiberglass backing that was present on the sample and was not attributed to degradation of the FEP material. There was also no change in dimension of any of the test coupons. Shore hardness for the samples is summarized in Table 5.2; with the exception of PVC, there was no significant change (i.e., >4) in hardness for any of the candidate materials of construction. Test results at 100 days or more will be compared with the hardness of PVC at 76 days to determine if this trend will have an impact on the selection

TABLE 5.2. Shore Hardness for Candidate Materials at Ambient Temperatures (Static Tests)

Candidate Material	Initial Hardness	Hardness After 76 Days Exposure					
		Case I	Case II	Case III	Case IV	Case V	Case VI
E-CTFE	76	77	77	75	76	78	78
TFE	58	61	60	60	61	61	61
PTFE	62	60	61	59	61	61	59
PVDF	79	81	82	83	83	82	80
FEP	61	59	--	61	61	60	59
PVC	80(a)	86	82	82	85	84	85
Polypropylene	74(a)	72	72	73	77	75	75

(a) Hardness after 1-day exposure to acid.

of materials for ambient temperature service in the reclamation system. Yellowing or deformation of the materials did not occur.

At the reference acid composition and elevated temperatures (100°C), the effects of temperature on each of the candidate materials was observed in laboratory-scale distillation unit. At this temperature, changes in appearance and in physical and mechanic properties occurred. After exposure to the acid for 1 day, the TFE coupon warped slightly and the E-CTFE coupon yellowed. The yellowing was no longer noticeable in the E-CTFE coupon after 35 days exposure. After 10 days exposure, the PVDF, TFE, and FEP coupons also warped slightly. Deformation was probably caused by the temperature. These phenomena may not affect the performance of the material in acid solution solutions at elevated temperatures, because a corresponding change in dimension, weight, or hardness was not observed. However, for the polypropylene and PVC samples, degradation occurred within the first 10 days of exposure to acid. Specifically, the polypropylene sample crazed when cut. The PVC sample had a 1% weight increase and embrittled. Embrittlement is indicated by an increase in the modulus of elasticity. Initially, the PVC coupon had a modulus of elasticity of 8360 psi; this increased to 12,600 psi after 10 days exposure. Therefore, the trends in this test indicated that polypropylene and PVC were not acceptable construction materials for service at elevated temperatures. The remaining materials appear to be satisfactory, but the modulus test will be run on materials exposed for 100 days to verify this conclusion.

The sets of coupons placed in the large bench-scale distillation system were exposed to the acid for only 10 days at the time of this report. Polypropylene and PVC coupons were not placed in the column because failure had already been observed in the laboratory-scale test at elevated temperatures. Consistent with observations of the materials at the elevated temperature in the laboratory-scale unit, the E-CTFE yellowed, and deformation/warpage of all candidate materials was observed. There was no change in weight, dimension, or hardness over this period of exposure with the possible exception of an apparent change of hardness of E-CTFE and PTFE coupons in the reboiler liquid. The laboratory-scale tests did not indicate a similar change; therefore, tests will continue to determine the significance of these changes. A summary of the hardness data is presented in Table 5.3.

5.3 PROCEDURE FOR DISTILLATION TESTS

The objective of the acid reclamation process is to reduce the volume of the waste acid ultimately requiring neutralization and disposal by reclaiming HNO_3 for recycle. A second objective is to reduce the concentration of NO_3^- in the final effluent. Because nitrates are mobile in the environment, their presence in a final waste form requires that more stringent performance criteria be used to ensure immobilization of the nitrate. With this increase in stringency, cost for final disposal will also increase. Therefore, it is desirable to reduce both the volume and quantity of nitrates in the final waste stream discharged from the reclamation process. These objectives can be met by using batch distillation to separate HNO_3 from the U-bearing $\text{HNO}_3\text{-H}_2\text{SO}_4$ (chemical milling solution). Similarly, HF can be recovered with the HNO_3 if it is present in the initial solution (i.e., chemical milling solution plus detoxified etch solution that can no longer be recycled).

Based on published vapor-liquid equilibrium for the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ternary system (Ellis and Thwaites 1957; Carpenter and Babor 1924), the chemical milling stream has sufficient H_2SO_4 to concentrate HNO_3 in the overhead vapor. An estimate of the recovery of HNO_3 as a function of overhead vapor composition that can be achieved by simple flash vaporization of the chemical milling

TABLE 5.3. Shore Hardness for Candidate Materials at Elevated Temperatures (Dynamic Tests)

Candidate Material	Initial Hardness	Hardness After 10 Days Exposure		
		Reboiler ^(a) Liquid	Reboiler ^(b) Vapor	Top of ^(c) Column
E-CTFE	76	81	77	78
TFE	58	60	55	59
PTFE	62	65	57	60
PVDF	79	83	80	82
FEP	61	62	60	61

(a) Combination of $\text{HF-HNO}_3\text{-H}_2\text{SO}_4$ in liquid phase.

(b) Combination of HF-HNO_3 in vapor phase.

(c) Combination of HF-HNO_3 in liquid and vapor phase.

stream is shown in Table 5.4 based on equilibrium data in Ellis and Thwaites (1957). Concentrated HNO_3 (57 wt%), which is typically used in fuel fabrication, can be produced directly by flash vaporization, and no additional distillation would be required. However, recovery of HNO_3 is only 75%. Higher recovery of HNO_3 can be achieved at the expense of a lower HNO_3 concentration in the overhead product. A rectification column would then be used to concentrate the HNO_3 .

Higher recovery of HNO_3 can also be achieved by adding H_2SO_4 to the solution. By increasing the H_2SO_4 concentration in the feed up to 60 wt%, it was estimated that 98% recovery of HNO_3 can be achieved as 57 wt% HNO_3 based on equilibrium data (Ellis and Thwaites 1957). In this operating scenario, the need for a rectification column to concentrate the HNO_3 has been eliminated and replaced by simple flash vaporization by adjusting the concentration of H_2SO_4 in the feed stream. Recovery and recycle of H_2SO_4 would probably be required, however, to achieve any net volume reduction of waste because of the addition of H_2SO_4 .

Laboratory tests were planned to verify these estimates with acid solutions that also contain HF. The distribution of HF between the overhead and bottoms cannot be determined from the literature, although it is believed that it will concentrate in the overheads (Stephenson, Hogan, and Kaplan 1984; Dasher and Goldstein 1963). In addition, temperature of the bottoms and

TABLE 5.4. Composition of Products from Flash Vaporization of Chemical Milling Stream

Overhead Product Concentration, wt% HNO_3 ^(a)	Fraction HNO_3 Recovered, %	Composition of Bottom Stream, wt% ^(b)		
		H_2SO_4	HNO_3	Solids ^(c)
57	75	50	8	12
50	95	62	2	14
45	~100	70	~0	16

(a) Assumes H_2SO_4 is not volatile.

(b) Remainder of bottom stream is water.

(c) Primarily UO_2SO_4 .

overhead streams, reduction in volume of acid disposed, concentration of F^- and NO_3^- in the bottoms stream, and concentration of SO_4^{2-} in the overhead stream were to be determined.

The approach taken was to conduct laboratory-scale equilibrium tests with a simple distillation unit. The feed streams added to the still pot are summarized in Table 5.5. Case I acid composition is that of the annual average composition of the chemical milling stream. Case II is the reference composition used in the corrosion tests that reflects the composition of the chemical milling stream plus the detoxified strip and etch solutions that can no longer be recycled. Cases III and IV are similar to Case II, but the concentration of H_2SO_4 in the initial acid makeup is increased to 40 wt% and 60 wt%, respectively. The procedure for distillation included placement of 250 mL of acid solution in the still. The solution was heated slowly, and temperatures of both the bottoms and overhead streams were taken as the distillation proceeded. Fractions of distillate were collected in a receiving flask and titrated to determine the total H^+ concentration. Ion chromatography (IC) was used to detect F^- , NO_3^- , and SO_4^{2-} in the first and last distillate fractions as well as the fraction with the highest total H^+ concentration.

5.4 DISTILLATION TEST TRENDS

The graphs shown in Figures 5.4 to 5.7 illustrate the results of the four distillation tests conducted at the time this report was prepared; additional tests are planned. Equilibrium data are also summarized in Table 5.6. Test results indicate that volume reduction during reclamation, fraction of HNO_3

TABLE 5.5. Composition of Acids Used in Equilibrium Tests

Case Number	HF	HNO_3	H_2SO_4	H_2O
I	--	19	32	49
II	0.1	21	28	50.9
III	0.1	21	40	38.9
IV	0.1	20.4	61.8	17.7

FIGURE 5.4. Concentration of Free Acid in Distillate Fractions from Case I Solution

FIGURE 5.5. Concentration of Free Acid in Distillate Fractions from Case II Solutions

FIGURE 5.6. Concentration of Free Acid in Distillate Fractions from Case III Solutions

FIGURE 5.7. Concentration of Free Acid in Distillate Fractions from Case IV Solutions

TABLE 5.6. Summary of Data from Equilibrium Tests

Case No.	Bottoms Temperature Range, °C	Distillate Temperature Range, °C	Fraction HNO ₃ Recovered, wt%	Fraction Original Volume, %	Avg. Conc. Overhead,	
					M	wt%
I	151-175	100-108	100	61	7.0	31
II	150-257	114-139	64	66	7.8	34
III	160-211	122-129	73	58	10.3	45
IV ^(a)	178-279	122-131	90	42	10.9	48

(a) NO_x formed in first distillate fractions collected.

recovered, and final composition of the distillate and bottoms streams are directly related to the initial acid composition fed to the batch distillation unit.

As can be seen in the figures, concentration of the H⁺ in the overhead distillate fractions reaches a maximum concentration before 100% of the HNO₃ is distilled. At higher initial H₂SO₄ concentrations in the feed stream, maximum HNO₃ concentrations in the distillate are reached in the first few fractions whereas at lower initial H₂SO₄ concentrations maximum HNO₃ concentrations in the distillate are reached in later fractions. In Table 5.7, the volume reduction (i.e., fraction of original volume) and the concentration of total H⁺ in the distillate are compared for three HF-HNO₃-H₂SO₄ mixtures (Cases II through IV) when 50 wt% nominal of the HNO₃ was recovered. Volume reduction decreased and concentration of acid in the overhead increased with increasing concentration of H₂SO₄ initially. The test results indicate that concentrated HNO₃

TABLE 5.7. Comparison of Equilibrium Data for 50% Recovery of HNO₃ in Distillate

Case No.	Bottoms Temperature Range, °C	Distillate Temperature Range, °C	Fraction HNO ₃ Recovered, %	Fraction Original Volume, %	Avg. Conc. Overhead,	
					M	wt%
II	150-170	114-127	50	50	8.2	36
III	160-172	122-127	51	30	13.8	61
IV	178-193	122-126	42	10	22.6	99

(i.e., concentrations greater than 57 wt%) can be recovered with a 20-30% volume reduction at higher initial concentrations of H_2SO_4 . Alternatively, more dilute HNO_3 , which would require rectification to generate 57 wt% HNO_3 for recycle, can be recovered with a 60-70% volume reduction; the more dilute HNO_3 is recovered from feed streams containing lower initial H_2SO_4 concentrations.

It was also observed that the temperature of the bottoms stream rose gradually with the first fractions of distillate but rose more sharply as the fraction of the original volume approached 60%. As the temperatures approached 175-190°C, sulfate ions were detected in the distillate fractions. Specifically, anion analysis was conducted for three distillate fractions for Cases I through III; these analyses were conducted on the first and last fraction collected as well as the fraction with the highest total H^+ concentration. In Table 5.8, it can be seen that sulfate was present in the last fractions, which were those taken at temperatures greater than 175°C. For Case I solution, which represents discharged chemical milling acid, 34 g/L sulfate was present in the distillate as 100% of the HNO_3 was recovered. This mixture could be recycled to the milling operations, but not to the stripping or etching operation because sulfate would prematurely attack the U during the process. The test result suggests that volume reduction and fraction of HNO_3 recovered would be decreased if 57 wt% HNO_3 free of H_2SO_4 was recovered for recycle. The options for recovering HNO_3 versus recovery of a mixture of HNO_3 - H_2SO_4 and subsequent recycle scenario will be selected based on an economic evaluation to be conducted after all the distillation test data are collected and evaluated.

TABLE 5.8. Anion Concentrations in Distillate Fractions

Case No.	Concentration, g/L									HNO ₃ ^(a) Recovered	Bottoms ^(a) Temperature
	First Fraction			Fraction with Highest [H-]			Last Fraction				
	F ⁻	NO ₃ ⁻	SO ₄ ⁻²	F ⁻	NO ₃ ⁻	SO ₄ ⁻²	F ⁻	NO ₃ ⁻	SO ₄ ⁻²		
I	-	109	-	-	332	2	-	35	34	100	175°C
II	2	152	-	2	609	-	-	60	8	62	222°C
III	4	625	-	2	554	-	<0.2	27	8	72	219°C

(a) Conditions listed are for final distillate fraction.

Finally, it was observed that HF readily distilled to the overhead stream in the first few distillate fractions. As shown in Table 5.8, F^- was detected in the first distillate fraction and the fraction containing the highest total H^+ , but not the fractions collected after 60% of the original volume was distilled. Although a complete mass balance cannot be made based on this data, the result suggests that HF was readily and completely vaporized. However, these laboratory-scale tests using a simple distillation unit without a packed column cannot indicate whether HF might concentrate in the column at some point. These data will need to be collected using the large bench-scale unit.

6.0 SUMMARY AND CONCLUSIONS

The following conclusions were made based on results of the bench-scale precipitation and distillation tests.

- Spent etch solutions comprising Zr-bearing HF-HNO_3 can be rejuvenated by precipitating the Zr as a zirconate salt using sodium fluoride as a precipitant. Concurrently, the HF is regenerated and the HF-HNO_3 mixture can be recycled to the etching operations to reduce the volume of waste acid generated from this metal-finishing process. The process was demonstrated on a large bench-scale system to determine those operating conditions that removed Zr by about 85% and produced a slurry with acceptable solid/liquid separation characteristics. The recommended operating conditions for this process include reaction temperature of 20°C or 60°C, impeller tip speeds of 320 cm/sec for adequate dispersal of solids, addition of NaF at 90% stoichiometry, and crystallization for a period of 24 h. Wetted surfaces of the reaction and separation equipment should be polypropylene or a fluoropolymer. A filter press provides acceptable separation of the reaction slurry before recycle of the acid.
- Spent stripping solution comprising Cu-bearing HNO_3 can be regenerated by precipitating the Cu as an oxalate salt using oxalic acid as a precipitant. Concurrently, the HNO_3 is regenerated and can be recycled to the stripping operations to reduce the volume of waste acid generated from this metal-finishing process. The process was demonstrated on a large, bench-scale system to determine the operating conditions that reduced the concentration of Cu by about 85% and still generated a slurry with acceptable solid/liquid separation characteristics. The recommended operating conditions for this process include a reaction temperature of 60°C, initial Cu concentration of up to 180 g/L, and crystallization for a period of 24 h. Seed solutions to enhance particle growth rate will not be needed. Wetted surfaces of this system should be polypropylene or a fluoropolymer. A pressure filter system will likely be needed for acceptable solid/liquid separation.

- Intermediate results from corrosion tests for candidate materials of construction for the acid reclamation system indicated that E-CTFE, TFE, FEP, and PVDF are suitable for wetted surfaces in contact with mixtures of $\text{HF-HNO}_3\text{-H}_2\text{SO}_4$ at ambient temperatures to temperatures of 100°C . Therefore, these materials appear to be acceptable for use in the heat exchange equipment and the rectification column. Polypropylene, PVC, E-CTFE, TFE, FEP, and PVDF can be used for wetted surfaces in contact with combinations of $\text{HF-HNO}_3\text{-H}_2\text{SO}_4$ at ambient temperatures. These tests will be continued to determine if degradation of materials occurs after exposure to the acid for longer than 100 days.
- Volume reduction during acid reclamation, fraction of HNO_3 recovered, and final composition of the distillate and bottoms streams are directly related to the initial composition of the acid mixture fed to the batch distillation system. It was observed that HF readily volatilized with the HNO_3 and it is unlikely that HF would remain in the bottoms stream. It was also observed that HNO_3 concentration in the distillate increased with increasing H_2SO_4 concentration in the initial feed stream, but that volume reduction correspondingly decreased. This result suggests that addition of H_2SO_4 to the feed stream may not be economically feasible unless H_2SO_4 can be recovered for recycle, because the primary economic incentive for use of the reclamation step will be volume reduction and subsequent reduction in cost for disposal. Finally, it was observed that H_2SO_4 distilled as the temperature of the bottoms stream exceeded 175°C . This result suggests that the fraction of HNO_3 recovered may be reduced if a HNO_3 stream free of SO_4^{2-} is needed for recycle. Alternatively, all of the HNO_3 can be recovered if H_2SO_4 can be tolerated in the recycle stream. For recycle to the milling solution, the mixture of $\text{HNO}_3\text{-H}_2\text{SO}_4$ would be acceptable, but sulfate cannot be present in the recycle stream to stripping or etching operations. The selection of recycle scenarios and operating conditions will be based at least in part on an economic evaluation conducted after further distillation tests are completed.

7.0 REFERENCES

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