A Research Report for
UNC Nuclear Industries, Inc.

**Evaluation of Improved
Chemical Waste Disposal
and Recovery Methods for
N-Reactor Fuel Fabrication
Operations: 1984 Annual
Report**

T. L. Stewart
J. N. Hartley

August 1985

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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ABSTRACT

Pacific Northwest Laboratory personnel identified and evaluated alternative methods for recovery, recycle, and disposal of waste acids produced during N Reactor fuel fabrication operations. This work was conducted under a program sponsored by UNC Nuclear Industries, Inc.; the program goals were to reduce the volume of liquid waste by rejuvenating and recycling acid solutions and to generate a residual waste low in nitrates, fluorides, and metals. Disposal methods under consideration included nitric acid reclamation, grout encapsulation of final residual waste, nitrogen fertilizer production, biodenitrification, chemical or thermal destruction of NO_3 , and short-term impoundment of liquid NO_3/SO_4 wastes. Preliminary testing indicated that most feasible and practicable of these alternatives were 1) nitric acid reclamation followed by grouting of residual waste and 2) nitrogen fertilizer production.

This report summarizes the investigations, findings, and recommendations for the 1984 fiscal year.

SUMMARY

In a program being conducted for UNC Nuclear Industries, Inc., Pacific Northwest Laboratory (PNL) personnel identified and evaluated alternative methods for recovery, recycle, and disposal of waste acids resulting from N Reactor fuel fabrication operations. The program goals were to evaluate on a laboratory-scale methods to 1) reduce the volume of liquid waste by rejuvenating and recycling acid solutions and 2) generate a residual waste low in nitrates, fluorides and metals.

Laboratory tests were conducted to help select the most technically feasible methods for rejuvenating spent acid solution at the source and for cleaning up waste acid solution before discharge. The candidate methods included precipitation, electrolysis, acid purification by resin bed exchange, and evaporation/distillation.

Literature on nitrate disposal and destruction was reviewed; additional information was obtained from personnel at the Oak Ridge National Laboratory (ORNL) Y12 facility and at the Kerr-McGee Nuclear Corporation (KMNC) Sequoyah facility. Disposal methods under consideration included: 1) nitric acid reclamation by distillation with H_2SO_4 to produce a low-nitrate waste, 2) grout encapsulation of final residual waste, 3) nitrogen fertilizer production, 4) biodenitrification, 5) chemical or thermal destruction of NO_3 , and 6) short-term impoundment of liquid NO_3/SO_4 wastes in the 300 Area of the Hanford Site. Preliminary laboratory tests were conducted for distillation, grout techniques, and fertilizer production.

Precipitation of principal metallic ions from spent acid solutions was determined to be the most feasible method for rejuvenation and cleanup of Zr-bearing $HF-HNO_3$ solutions and Cu-bearing HNO_3 solutions. Zirconium was precipitated as calcium or sodium hexafluozirconate by adding solid CaO , $Ca(OH)_2$, $CaCO_3$, CaF_2 , NaF , $NaOH$, and $NaNO_3$. Sodium compounds were preferred to avoid downstream fouling in distillation units and product dilution during uranium recovery. The most promising precipitant in the preliminary tests was NaF . At ambient temperature and 95% stoichiometry, the concentration of Zr was reduced

from 37 g/L (0.31 lb/gal) to 4 g/L (0.03 lb/gal) while maintaining acid concentration. This process is patented by Teledyne Wah Chang.

Results of the Zr precipitation tests using NaOH were unexpectedly poor due to a limiting concentration of HF. A German patent issued on this process suggested that reevaluation of NaOH as a precipitant was warranted. The use of NaOH has two benefits: 1) waste HF is consumed and 2) NaOH is routinely handled on site. Water is produced in the reaction, diluting the recycle stream. Therefore, a bleed stream and makeup acid will be required to maintain acceptable acid concentration.

Copper precipitation can be accomplished by adding oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), Na_2CO_3 , or NaOH to the acid solution. In an ammonia-cal solution, Cu, in dilute concentrations, can be precipitated as an oxide with steam or heat. Preliminary laboratory tests were conducted to determine which precipitant selectively removed Cu, leaving U in solution for recovery during downstream neutralization.

Addition of oxalic acid was the most feasible method of rejuvenating the copper strip solution; nitric acid is regenerated and Cu is removed from solution as an oxalate. At 100% stoichiometry and temperatures above 35°C, 97% of the HNO_3 was returned and the Cu concentration was decreased from 157 g/L (1.31 lb/gal) to 0.5 g/L (0.004 lb/gal). Elevated temperatures were required to increase the solubilization of oxalic acid.

Addition of sodium oxalate was the most feasible method for cleaning up waste acid from the combined Cu strip and Cu rinse streams before neutralization and discharge. Acid was not regenerated with Na oxalate addition; therefore, stream cleanup can be achieved with no additional neutralization requirements. Copper concentration was reduced from 118 g/L (0.98 lb/gal) to 0.1 g/L (0.008 lb/gal).

High-current-density electrowinning was another method investigated for rejuvenation of the Cu strip solution and cleanup of combined Cu strip and Cu rinse solution. Continuous acid rejuvenation was demonstrated on a laboratory scale. At electrolyte temperatures of 5 to 10°C, a continuous system of Cu stripping and electrowinning was operated for 32 hours. A steady-state stream

composition of 3.5 M HNO_3 and 100 g/L (0.83 lb/gal) Cu was maintained. Current density was 0.19 A/cm^2 (177 ASF) with current efficiency reaching 70%. About 55% of the HNO_3 was regenerated.

Sulfamic acid was added to the electrolyte during the electrowinning operation to clean up waste acid from Cu strip and Cu rinse solutions. Copper concentration was reduced from 98 g/L (0.82 lb/gal) to 4 g/L (0.03 lb/gal). At 0.11 A/cm^2 (100 ASF), the current efficiency dropped from 90% to 20% during the Cu depletion run. The energy consumption remained constant due to a decreasing voltage drop in the electrolyte with decreasing Cu concentration.

Acid purification by resin bed exchange was another method tested for rejuvenating Cu strip solution. Results show that 30% of the Cu and 1% of the HNO_3 were removed from the Cu strip solution by this treatment. However, tests were hampered by stream pretreatment problems; gelatinous silicic acid, which could plug the resin bed, was difficult to remove.

After reviewing the alternative waste acid disposal methods, we selected two methods of waste acid disposal for further investigation: 1) nitrate reclamation with distillation followed by grouting of residual waste (low-nitrate waste process) and 2) nitrogen fertilizer production. Preliminary distillation, grout, and fertilizer tests were performed. Bionitrification may be a feasible alternative to grout encapsulation for the treatment of low-nitrate wastes. Chemical and thermal nitrate destruction show promise, but the techniques have not yet been fully demonstrated. Improved impoundment techniques may be less feasible. Proposed regulations for construction of new ponds are changing rapidly. As a result, there are several unknown contingency factors that could drive construction costs upward.

Preliminary distillation tests were conducted with samples of spent HF-HNO_3 from a Zr etch solution, spent HNO_3 from the Cu strip solution, aqueous sodium nitrate wastes, and spent $\text{HNO}_3\text{-H}_2\text{SO}_4$ from the U milling solution. Several qualitative observations were made. Nitric acid was readily distilled to the overhead stream. Concentration of HNO_3 in the distillate was dependent on the initial concentration of H_2SO_4 in the still pot. Sulfate concentration in the distillate increased after most of the nitrate had distilled over; a

corresponding temperature rise in the distillate was observed. Nitrate concentration in the bottoms could be reduced to 0.9 g/L (0.008 lb/gal).

Preliminary grout tests were completed with the NaNO_3 waste slurry discharged. Grout was made from both the waste supernate and the slurry waste. The supernate formed an acceptable grout; both setup rate and strength were within defined limits. The mixed (slurry) waste did not set up. More formulation testing would be required to develop an acceptable mix.

The second disposal method studied was production of nitrogen fertilizer from waste nitric or nitric/sulfuric acid. Ammonium hydroxide is the neutralizing agent; U is recovered during neutralization as a diuranate. The resulting ammonium nitrate/sulfate solution can be used as fertilizer. A similar procedure has been developed over the last 10 years by KMNC.

Fertilizer produced from the acid waste would contain low concentrations of Cu, U, and Tc-99 after NH_4OH neutralization and solids separation. Chelating resins could reduce the Cu and U concentrations to an acceptable level in a final polishing step. Preliminary tests using anion exchange resins or precipitation techniques to remove Tc-99 were completed. Anion exchange resins reduced the Tc-99 to an environmentally acceptable level (<0.0174 mg/L, Tc maximum limit). Precipitation of Tc as a sulfide did not reduce the Tc concentration to an acceptable level.

Results of the preliminary tests indicated that the following methods for rejuvenation, recycling, and disposal may be beneficial if incorporated into the proposed UNC chemical waste process:

- HF-HNO_3 rejuvenation and cleanup by precipitating Zr with NaF or NaOH
- HNO_3 rejuvenation in the copper strip solution by precipitating Cu with oxalic acid
- cleanup of the waste Cu-bearing stream with $\text{Na}_2\text{C}_2\text{O}_4$
- reclamation of nitrates and fluorides by distillation with H_2SO_4
- disposal of the residual sulfate waste by grouting.

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INTRODUCTION

The N Reactor fuel fabrication operation, managed by UNC Nuclear Industries, currently generates a neutralized waste slurry that is discharged to solar evaporation basins. The liquid portion of the slurry contains soluble nitrates and fluorides as well as minor concentrations of U, Tc-99, and other hazardous chemicals. Improved chemical waste disposal and recovery methods were identified and evaluated by Pacific Northwest Laboratory (PNL)^(a) personnel for UNC.

Alternative methods for disposing of spent acids resulting from fuel fabrication have been identified and preliminary studies on the technical feasibility of proposed methods have been completed. Initially, a system was considered in which impurities such as U and Cu were to be recovered or removed from waste acid solutions before disposal with no reduction in waste volume. As the work proceeded, it became evident that disposal cost was the dominant economic factor in alternative process concepts. Therefore, the final waste system design had to include methods for reducing the volume of liquid effluent, removing or recovering metals and acids, and disposing of the waste in accordance with DOE, EPA, and state requirements.

Three primary waste streams are produced during N Reactor fuel fabrication: a U-bearing stream, which contains nitric and sulfuric acid; a Cu-bearing stream, which contains HNO_3 ; and a Zr-bearing stream, which contains HF-HNO_3 (see Figure 1). Minor impurities include Tc-99, Be, Cr, Fe, Ni, and Si. Currently, the acid baths are used until the concentration of major impurities exceeds acceptable operating limits. The solutions are then discharged, neutralized with NaOH, and transported to 100 H Area solar evaporation

(a) Operated for the DOE by Battelle Memorial Institute.

FIGURE 1. Conceptual Flow Diagram of Waste Acid Resulting from Fuel Fabrication

basins for storage. Uranium is recovered during neutralization as a sodium diuranate precipitate, but large quantities of acid and metals that can be recovered are handled as waste.

Several process options that would meet the overall waste acid process design requirements were studied. Acid recycle of Zr-bearing streams by precipitation of Zr was included in all the design options. Recycle of Cu strip solution by removing Cu and regenerating HNO_3 electrolytically or chemically by precipitation was also included in all options. Grout encapsulation and impoundment were studied as potential interim disposal methods to be used until 1988, which is the projected date of startup for the complete chemical waste system. Long-term disposal plans were studied, including NO_3 recovery by distillation and grouting of the resulting SO_4 waste, conversion of the NO_3/SO_4 waste to nitrogen fertilizer, biodenitrification in stirred-bed reactors, and chemical or thermal destruction of waste nitrates.

Laboratory experiments were designed to investigate the technical feasibility of methods either to clean up a waste stream before disposal or to rejuvenate a spent acid solution before recycle. Techniques studied included 1) precipitation, 2) electrolysis, 3) acid purification by resin bed exchange, and 4) evaporation/distillation. Specifically, PNL staff conducted preliminary investigations of the following:

- precipitation of Zr from spent HF-HNO₃ with NaF, CaF₂, NaNO₃, NaOH, CaO, Ca(OH)₂, and CaCO₃ for cleanup or recycle of Zr etch baths
- precipitation of Cu in dilute concentrations with oxalic acid (H₂C₂O₄), Na₂CO₃, steam or heat for final stream polishing
- precipitation of Cu from undiluted spent acid with H₂C₂O₄ and sodium oxalate (Na₂C₂O₄) for recycle of the Cu strip solution (tank 10)
- precipitation of Cu from undiluted spent acid with H₂C₂O₄, Na₂C₂O₄, Na₂CO₃, and NaOH for cleanup of the Cu strip solution and Cu rinse water (combined tanks 10 and 25)
- precipitation of Tc-99 as a sulfide with H₂S from ammoniacal waste
- anion exchange removal of Tc-99 in an ammoniacal waste
- electrolytic removal of Cu from a HNO₃ solution containing sulfamic acid for stream cleanup
- electrolytic recovery of Cu and regeneration of HNO₃ at reduced electrolyte temperatures for stream recycle
- distillation of nitric acid from spent Cu strip (tank 10) solution
- distillation of HF-HNO₃ from spent etch (tank 15) solution
- distillation of HNO₃ from the NaNO₃ waste after sulfuric acid addition
- acid regeneration of Cu strip (tank 10) solution by acid purification in a resin bed exchange unit
- waste encapsulation of the NaNO₃ wastes in a grout.

PNL staff also reviewed information on the production of ammonium nitrate/sulfate fertilizer from waste acids neutralized with NH_4OH , biodenitrification, thermal and chemical destruction of nitrates, and waste impoundment in the 300 Area.

Results of the laboratory investigations conducted during FY 1984 are summarized in the following sections.

RECOMMENDATIONS

Laboratory and engineering development activities are needed to help select and optimize improved chemical waste disposal and recovery methods. Specific recommendations are:

- Optimize Zr precipitation from HF-HNO₃ and Cu precipitation from HNO₃ streams.
- Evaluate methods for HF removal from waste acid before centrifugation or distillation.
- Optimize operating parameters for a distillation system.
- Test materials of construction for an evaporator and distillation column.
- Evaluate disposal methods for residual SO₄ waste in the low-nitrate waste process.
- Evaluate disposal techniques for all solid wastes.
- Evaluate methods to remove Tc-99 and metallic cations from by-product fertilizer.^(a)
- Conduct pilot plant operation to produce fertilizer to be tested in greenhouse and field studies.^(a)
- Evaluate biodenitrification as a final effluent cleanup step.
- Determine equipment requirements and prepare preliminary engineering specifications for each waste process.

(a) These activities are recommended if UNC selects the fertilizer production process as part of the chemical waste system.

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PRECIPITATION

Precipitation of Zr from HF-HNO₃, of Cu from HNO₃, and of Tc-99 from ammoniacal wastes was investigated as a possible technique for acid recycle and for waste stream cleanup. Several precipitants were identified. Preliminary laboratory tests were conducted to determine the more promising reagents for further testing. Preliminary information on process conditions was also gathered.

Zr PRECIPITATION

The primary objective of laboratory-scale precipitation tests for Zr removal or recovery was to identify precipitants that could reduce Zr concentrations in HF-HNO₃ solutions before recycle or discharge of the stream. A secondary objective was to determine the concentration of F remaining in solution after precipitation. The F concentration will indicate the amount of makeup HF required for a recycle stream and will dictate the choice of materials for downstream process units.

Background

Tanks 5, 13, 15, 19, and 26 contain aqueous HF-HNO₃ solutions used as Zr etch baths in the fuel fabrication process. Tanks 15, 19, and 26 are dumped frequently as the concentration of Zr approaches 35 g/L (0.29 lb/gal). Concentrations of HF and HNO₃ are maintained between 17 to 22 g/L (0.14 to 0.18 lb/gal) HF and 360 to 432 g/L (3.0 to 3.6 lb/gal) HNO₃ by adding makeup acid during Zr dissolution. The volume of combined streams is 2×10^5 L/yr (53,360 gal/yr). Recycling after Zr removal and acid rejuvenation could reduce this waste volume to less than 1×10^4 L/yr (2700 gal/yr).

Since fluozirconates are very insoluble in HF-HNO₃ solutions, Zr can be removed from an acid etch solution by precipitation with soluble Ca, Na, or K. Rejuvenated acid can be recycled until the concentration of minor impurities such as Be, Cr, U, or Cu exceeds acceptable operating limits. Teledyne Wah Chany has a patent (Megy et al. 1978) on an acid recycle process for Zr-bearing HF-HNO₃ solutions using NaF as the precipitant; until recently, the system had been used at the facility at Albany, Oregon. In this process, crystalline NaF

is added to HF-HNO₃ solutions containing about 30 g/L Zr at 95% Zr stoichiometry to reduce Zr concentration in the recycle stream to 3 to 7 g/L. The solution is stirred for 30 minutes and then allowed to stand undisturbed for 3 to 4 h. The solution is remixed and filtered; the acid supernate is recycled to the etch tanks, and the slightly acidic Na₂ZrF₆ precipitate is dried and released for burial or resale to the aluminum industry.

Several Na or Ca compounds could be used to remove Zr from HF-HNO₃ solutions; CaF₂, CaO, CaCO₃, Ca(OH)₂, NaF, NaOH, and NaNO₃ were identified as candidate precipitants. Both Zr and F are removed from solution according to the following reactions:

Use of NaOH as a precipitant to form Na₂ZrF₆ and to rejuvenate HF-HNO₃ solutions is described in a German patent (Fennemann 1981).

Experimental Procedure

Laboratory-scale tests for the Ca and Na compounds were conducted at different times and with different tank solutions. The CaO, CaCO₃, and Ca(OH)₂ tests were run with a sample of tank 19 solution and the remaining tests were run with a sample of tank 15 solution. Tank 15 had a lower HF and a higher Zr concentration than expected. Compositions are shown as feed concentrations in

Tables 1 through 3. Experiments were conducted at room temperatures initially; temperature was varied for some later runs. Tests with CaF_2 , NaF , NaOH , and NaNO_3 followed the same procedures as those outlined in the Wah Chang patent; solid precipitant was added as the solution was stirred, stirring continued for 30 minutes, and the precipitate was then allowed to settle for 3 to 4 h. Stoichiometry was varied in some runs. Separation was accomplished by settling, centrifuging, and vacuum filtration. Samples were taken from the supernate to determine cation concentrations with inductively coupled plasma (ICP) analysis.

TABLE 1. Concentration of Ionic Species After Precipitation of Zr with Calcium Oxide, Hydroxide, and Carbonate at 100% Stoichiometry

Cation	Feed Concentration, ppm	Filtrate Concentration, ppm			Percent Reduction		
		CaO	Ca(OH)_3	CaCO_3	CaO	Ca(OH)_2	CaCO_3
Al	424	22	15	1	94.8	96.5	99.8
Be	9	1	1	1	88.9	88.9	88.9
Cr	115	14	26	1	87.8	77.4	99.1
Fe	369	24	30	1	93.5	91.9	99.7
Ni	57	0	0	54	100.0	100.0	5.3
Si	9,833	0	0	0	100.0	100.0	100.0
Zr	24,530	173	2,010	10	99.3	91.8	99.9

TABLE 2. Concentration of Zr After Precipitation with CaF_2 at 95% Stoichiometry and 0°C, 20°C, and 40°C

Cation	Feed Concentration, ppm	Filtrate Concentration, ppm			Percent Reduction		
		0°C	20°C	40°C	0°C	20°C	40°C
Al	300	270	320	310	0	0	0
Cr	75	70	66	66	7	12	12
Cu	110	100	97	100	9	12	9
Fe	220	200	190	180	9	14	18
Ni	36	36	34	33	0	6	8
Si	9,815	7,400	7,300	7,800	25	26	21
Zr	37,100	10,500	19,200	34,600	72	48	7

TABLE 3. Concentration of Zr and Na After Precipitation with NaNO_3 and NaOH (a)

Precipitant	Stoichiometry, % of Zr	Temperature, °C	Feed Concentration, g/L		Filtrate Concentration, g/L		Percent Reduction Zr
			Zr	Na	Zr	Na	
NaNO_3	75	20	37	0	24.0	3.5	35.0
	100	"	"	"	23.0	6.3	37.8
	100	40	"	"	23.7	6.6	36.0
	200	20	"	"	23.3	22.4	37.0
NaOH	75	20	"	"	2.2	1.4	94.1
	95	"	"	"	13.3	2.7	64.1
	100	"	"	"	11.9	3.3	67.8
	150	"	"	"	11.8	8.1	68.1
	200	"	"	"	33.5	21.7	9.5
	75(b)	"	"	"	33.0	3.6	10.8
	200(b)	"	"	"	31.6	22.7	14.6

(a) Complete results are given in Appendix A.

(b) Repeated tests.

Results and Discussion

At 100% stoichiometry and room temperature, the concentrations of Zr and F were reduced by up to 99.9% and 99.8%, respectively, with CaO , Ca(OH)_2 , and CaCO_3 . The results, shown in Table 1, indicated that any of these Ca compounds could be used to reduce Zr and F concentrations. However, downstream process problems could occur for the proposed UNC waste systems. First, water is formed in each of these precipitation reactions and the recycle stream is diluted. A bleed stream and makeup acid would be required to maintain the acid concentration within acceptable operating ranges. Second, Ca would increase fouling problems in downstream distillation units because SO_4 ions are present. Third, excess Ca would form insoluble CaSO_4 when this stream was mixed with the U-bearing stream containing H_2SO_4 , which would dilute the Na diuranate precipitated during neutralization.

At 95% stoichiometry and 0°C , CaF_2 reduced Zr concentration to 10.5 g/L, but at higher temperatures Zr reduction decreased as shown in Table 2. CaF_2 could be used for acid rejuvenation since no water is formed in the reaction. The process would require a chiller to maintain the low stream temperature, however, which would increase equipment and operating costs. Also, the downstream problems of fouling and dilution would result.

Results of precipitation tests using NaOH and NaNO_3 were inconclusive. NaOH was added at 75%, 95%, 100%, 150%, and 200% stoichiometry in the first set of experiments. As shown in Table 3, anomalous results were obtained. Tests for addition of 75% and 200% of stoichiometry were repeated; more consistent results were obtained, but the Zr reduction was less than expected. A mass balance indicated that HF was a limiting reactant due to low HF and high Zr concentrations for this particular tank 15 sample. The calculated average concentration of HF in tank 15 indicated that HF should be available in excess. However, a range of HF and Zr concentrations will exist in the batch operation and solution analysis before precipitation will be necessary for this system to operate efficiently. Reduction of Zr concentrations in solutions treated with NaNO_3 was also less than expected, for the same reason. Time considerations did not allow a repeat of the tests.

Because a patent was issued on the NaOH process under process conditions similar to those of fuel fabrication, it can be assumed that this precipitant will yield satisfactory results. As shown in Equation 6, water is formed; the recycle acid would be diluted from 6.85 M HNO_3 (3.6 lb/gal) to 4.38 M HNO_3 (2.3 lb/gal) before discharge, assuming 20 recycles. A bleed stream and makeup acid will be required for this operation. On the other hand, NaNO_3 should produce a solution with increased acid concentration since HNO_3 is produced (see Equation 7). Although some of this acid would replace the nitric acid lost through the dissolution of impurity metals, a bleed stream would probably have to be incorporated into the process design to maintain a constant HNO_3 concentration.

At 95% stoichiometry, the concentration of Zr was reduced from 37.1 to 4.2 g/L at 20°C when NaF was used as a precipitant. Information in the Wah Chang patent indicates that similar results can be expected at the elevated temperatures at which the actual tank solutions are maintained. Water is not produced in the reaction and the recycle stream is not diluted (see Equation 5). Sodium ions would not cause downstream fouling of distillation units.

Conclusions

The investigation of Zr precipitation produced the following conclusions:

- 1) NaF reduced the concentration of Zr at room temperature without diluting the acid solution.
- 2) Further work needs to be done with the NaOH and NaNO_3 system, but in either system the acid concentration levels will have to be maintained by bleed streams.
- 3) Ca precipitation may cause downstream process problems.
- 4) F^- concentration can be significantly reduced by precipitation with CaO , Ca(OH)_2 , and CaCO_3 in an acid solution.
- 5) Further investigation of the possible buildup of minor metal impurities in the recycled HF-HNO_3 stream is required.
- 6) Solid/liquid separation was successful by settling, centrifuging, and vacuum filtration.

Cu PRECIPITATION

The primary objectives were to determine the most feasible precipitant for cleanup of the Cu-bearing stream before neutralization and the most feasible precipitant for Cu removal and acid rejuvenation in a recycle stream to the Cu strip tank. Uranium found as a minor impurity in the Cu streams was to remain in solution as Cu was selectively removed to a concentration of 4200 mg/L Cu; U was to be recovered as a diuranate in a later process step. The maximum limit of 4200 mg/L Cu in the filtrate was acceptable to the U diuranate processor. This limit was arbitrarily chosen as the maximum concentration of Cu in the recycle stream as well.

Background

Copper precipitation appeared to be a viable method for Cu-bearing stream cleanup or acid waste rejuvenation for solution recycle. Experiments were conducted with samples of UNC Cu strip solution from tank 10 and Cu rinse water from tank 25. These waste streams contained Cu and U in aqueous HNO_3 . In

initial screening tests, solutions containing low concentrations of Cu were used, in order to simulate the polishing of an effluent stream treated first by electrolysis. Later, tests were run to determine the efficiency of Cu removal from undiluted tank 10 for spent acid rejuvenation and waste acid cleanup. The goal for each set of experiments was to precipitate the Cu without coprecipitating U.

Several possible precipitants were identified including $\text{H}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{C}_2\text{O}_4$, NaOH , Na_2S , or Na_2CO_3 for use in an acid solution; the precipitation reactions are shown below:

Steam can be used to precipitate CuO from a basic solution.

Experimental Procedure

Screening tests were conducted for $\text{H}_2\text{C}_2\text{O}_4$, Na_2CO_3 , Na_2S , and steam on diluted samples of the Cu strip solution (tank 10). Later, more tests were run with $\text{H}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{C}_2\text{O}_4$, Na_2CO_3 , and NaOH on undiluted Cu-bearing waste acid (tanks 10 and 25). All runs were initially conducted at room temperature. For the screening tests, tank 10 solution containing 4.0 N HNO_3 and 157 g/L Cu was diluted to about 0.6 g/L, 6 g/L, and 63.5 g/L Cu. Excess precipitant was added to 50-mL samples of these solutions. Steam was bubbled through 50-mL samples of solutions containing 0.6, 6, and 63.5 g/L Cu which had been neutralized with NH_4OH . For one test, a 6-g/L Cu solution was heated by bubbling steam through the solution, CuO was added to seed the precipitation, and then NH_4OH was added as steam was bubbled into the solution. In later tests, $\text{H}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{C}_2\text{O}_4$,

Na_2CO_3 , and NaOH were added to undiluted tank 10 solution, undiluted tank 25 solution, and a combined solution of tanks 10 and 25. Since $\text{H}_2\text{C}_2\text{O}_4$ did not go into solution well, some tests were run using ultrasound for 15 min and other tests were run at elevated solution temperatures to determine which method would ameliorate the solubilization problem. All solutions were mechanically stirred as the solid precipitant was added. Stoichiometry was varied for $\text{H}_2\text{C}_2\text{O}_4$ tests. Separation was achieved by vacuum filtering, centrifuging, and settling. Copper concentration was determined by atomic absorption (AA) spectroscopy, U concentration was determined by U fluorimetry, and H ion concentration was determined by titration against NaOH .

Results and Discussion

In the screening tests, the concentration of Cu was reduced by all the precipitants. Results are shown in Table 4; the reported Cu and U concentrations in the filtrate are average concentrations for samples to which excess precipitant was added.

TABLE 4. Concentration of Cu and U After Precipitation with Oxalic Acid, Sodium Carbonate, and Steam in the Screening Tests

Precipitant	Feed Concentration, mg/L		Filtrate Concentration, mg/L		Final pH
	Cu	U	Cu	U	
$\text{H}_2\text{C}_2\text{O}_4$	690	6	57	6	1.2
	7,660	81	35	40	0.6
	65,800	920	81	465	--
	157,000	1,550	83	528	--
Na_2CO_3	690	6	13	4	10.4
	7,660	81	290	17	9.1
Steam (basic solution)	690	6	38	0.0006 ^(a)	9.7
	7,660	81	56	0.98 ^(a)	10.4
	63,500	-	no precipitation	-	9.5
Steam ^(b)	7,660	-	60	-	3.5

(a) U removed during neutralization with NH_4OH .

(b) Solution was heated by bubbling steam through the sample, CuO was added to seed the precipitation, and then the hot solution was neutralized with NH_4OH .

Oxalic acid produced the best results in the screening test. Independent of initial Cu concentration, the concentration of Cu in the filtrate was reduced to an average of 58 mg/L as a low pH was maintained. Sodium carbonate also reduced Cu concentration but the final solution pH was above 9.0; the pH would have to be adjusted to recover the U. Steam efficiently removed Cu at low Cu concentrations only; this technique could be used to polish the ammonia-cal stream. A yellow film, which was difficult to remove, formed on the glassware and was suggestive of potential fouling problems. Note that a low pH was measured for the solution initially containing ~6 g/L Cu (7660 ppm) in which the solution was neutralized after being heated with steam and seeded with CuO. As can be seen in Table 4, the concentration of U appeared to be reduced by all precipitants. However, these results were questionable due to operating problems with the U analyzer.

Further laboratory-scale tests were conducted with $H_2C_2O_4$, $Na_2C_2O_4$, and Na_2CO_3 as precipitants in undiluted tank 10 solutions. For comparison, some samples were also treated with NaOH. The results are shown in Tables 5 and 6 and in Appendix A.

TABLE 5. Results of Oxalic Acid Precipitation of Copper from Tank 10 Solution

Test	Stoichiometry	Temperature, °C	After Precipitation		
			Cu ⁺⁺ , ppm	U, ppm	H ⁺ , Molarity
Tank 10(a)	--	--	168,000	1571	4.5
T10-I	50	30	77,000	1159	7.2
T10-II	75	33	49,300	1623	8.2
T10-III	100	35	4,800	1268	9.4
T10-IV	100	28	84,500	1023	6.5
T10-V	100	33	29,900	1270	8.0
T10-VI	100	39	333	1363	9.2
T10-VII	100	56	111	1486	9.2
T10-VIII	100	95	2,580	---	9.6

(a) Sample of tank 10 as received (i.e., initial solution composition).

TABLE 6. Results of Precipitation Tests Using Tank 25 and Combined Solutions at 100% Stoichiometry

Test	Reagent	Average Temperature, °C	Remaining Cu++, ppm	H+, Molarity
<u>Tank 25 Tests</u>				
Tank 25	Stock	25	5,080	1.3
T25-I	Na ₂ C ₂ O ₄	25	1,050	1.5
T25-II	Na ₂ C ₂ O ₄	63	780	2.0
T25-III	Na ₂ CO ₃	24	95	1.41e ⁻⁶ (pH = 5.85)
T25-IV	Na ₂ CO ₃	59	1,860	5.01e ⁻⁶ (pH = 5.30)
T25-V	NaOH	28	470	6.31e ⁻⁶ (pH = 5.20)
T25-VI	NaOH	68	310	7.94e ⁻⁶ (pH = 5.10)
<u>Combined Tank 25, Tank 10, and Rinse Water Tests</u>				
Combined	Stock	25	118,000	3.2
TC-I	Na ₂ C ₂ O ₄	28	2,540	3.2
TC-II	Na ₂ C ₂ O ₄	68	4,750	3.4
TC-III	Na ₂ CO ₃	31	53	5.01e ⁻⁹ (pH = 8.3)
TC-IV	Na ₂ CO ₃	58	30	6.31e ⁻⁶ (pH = 5.2)
TC-V	NaOH	64	7.4	3.16e ⁻⁶ (pH = 5.5)
TC-VI	NaOH	77	6.7	7.94e ⁻⁶ (pH = 5.1)

Oxalic acid reacted almost completely (97%) with Cu in the strip solution (tank 10). Nearly two moles of H⁺ were generated for each mole of Cu precipitated. These results indicated that Cu and acid concentrations in the recycle stream can be controlled precisely by adding oxalic acid at slightly less than 100% stoichiometry.

The most pronounced factor affecting the precipitation of Cu with H₂C₂O₄ was temperature. Table 5 shows the abrupt change in Cu concentration in the filtrate as the solution temperature exceeds 35°C; above this temperature, the Cu concentration decreases to less than 500 ppm. Normal operating temperatures for tank 10 range from 38 to 65°C, which would be ideal for Cu removal with H₂C₂O₄. Higher temperatures are also favorable for keeping U in solution during Cu precipitation. Nearly one-third of the U precipitated at 28°C while

only a minor amount precipitated at 56°C. Ultrasound appeared to aid solubilization, but the effect was probably due to an increase in solution temperature resulting from heat dissipation of ultrasonic energy.

Although Cu concentration during stream cleanup can be greatly reduced by adding $\text{Na}_2\text{C}_2\text{O}_4$, Na_2CO_3 , or NaOH to tank 25 or combined tanks 10 and 25, only $\text{Na}_2\text{C}_2\text{O}_4$ precipitation of Cu produces a supernate with a low pH; a low pH allows for U recovery as a diuranate after the cleaned Cu-bearing stream is mixed with the U-bearing stream for neutralization. Unlike precipitation with $\text{H}_2\text{C}_2\text{O}_4$, pH is maintained; this will reduce the amount of neutralizing agent required in following process steps.

Copper oxalate may not be suitable for disposal due to its toxicity and slight solubility in water. It can be converted, however, to CuO by heating the solid to about 200°C in an oven.

Conclusions

The following conclusions were derived from results of the Cu precipitation investigation:

- 1) Oxalic acid can be used to remove Cu as an oxalate and to regenerate HNO_3 for recycle of the waste acid stream from the Cu strip tank.
- 2) Solution temperatures above 35°C would allow solid $\text{H}_2\text{C}_2\text{O}_4$ to go into solution. Since tank solution temperatures will be greater than 35°C, minimal temperature control should be required to precipitate Cu with $\text{H}_2\text{C}_2\text{O}_4$.
- 3) Sodium oxalate can be used as a precipitant for cleanup of the combined Cu-bearing streams, since copper concentration is reduced well below the specified limits and pH is maintained to reduce the amount of neutralizing agent required.
- 4) Uranium appeared to remain in solution, particularly at higher solution temperatures, for recovery in a later process step.

- 5) Steam could be a viable method of removing very low concentrations of Cu from the ammoniacal solution intended for use as a fertilizer.

Tc-99 PRECIPITATION

It was found that Tc-99 was present in the U-bearing waste acid. In order for the waste to be used as a nitrogen fertilizer, the Tc-99 has to be removed to a maximum of 300,000 pCi/L, the concentration limit for release of Tc-99 to an uncontrolled area. Two possible methods of Tc removal were identified and evaluated. First, anion exchange resins have been routinely used in the nuclear industry to remove Tc. Preliminary laboratory studies to determine the number of column volumes before breakthrough were conducted by C. L. Matsuzaki. Results are included in her report to E. A. Weakley on March 9, 1984 (see Appendix C). Second, Tc-99 can be removed by precipitation with H_2S to form Tc_2S_7 . A preliminary lab test was carried out to determine the concentration of Tc-99 after excess H_2S was bubbled through an ammoniacal solution of combined tanks 32 (Chemical Milling) and 16 (Billet Etch).

Experimental Procedure

A feed solution containing U-bearing waste solutions from tanks 32 and 16 was prepared; the mixture contained 91% tank 32 and 9% tank 16 by volume. The solution was neutralized with NH_4OH . A gross beta count was taken to determine the concentration of Tc-99 before and after precipitation. Three bubblers were connected in series so that H_2S was bubbled through the test solution in the first container and then excess H_2S bubbled through a 5% zinc acetate solution and a Cd salt solution. The latter containers absorbed and indicated the presence of excess H_2S by changes in the physical properties of the solutions. H_2S was bubbled through the ammoniacal solution in excess.

Results and Discussion

Initially the solution contained 0.354 mg/L Tc-99 and after precipitation with H_2S , the solution contained 0.0352 mg/L Tc-99. This concentration would still be too high for release to an uncontrolled area even after dilution with the remaining neutralized waste streams. It was suggested that this experiment be rerun after seeding the solution with Mn for coprecipitation.

ELECTROWINNING

The electrolytic removal of Cu and regeneration of HNO_3 from the Cu strip solution or the combined Cu strip/Cu rinse solution was investigated as a possible technique for acid recycle or acid waste cleanup. In FY 1983, preliminary studies indicated that Cu could only be removed from a concentrated ($>1.0 \text{ M HNO}_3$) nitric acid solution if the electrolyte was cooled below 15°C to decrease the rate of the competing chemical dissolution reaction or by adding sulfamic acid to destroy the NO_2 ions that catalyze the dissolution reaction. A current efficiency greater than 90% can be achieved with sulfamic acid addition and Cu concentrations can be reduced to less than 4.2 g/L, the requirements for stream cleanup. However, residual SO_4 , which attacks uranium, makes this technique unacceptable for acid recycle. Compared to the sulfamic acid addition method, a lower current efficiency was achieved by cooling the electrolyte, but this technique can be used for acid recycle. Therefore, laboratory investigations were conducted to determine the operating parameters required to treat the Cu strip solution for recycle at reduced electrolyte temperatures and to treat the combined Cu strip/Cu rinse solution for stream cleanup before discharge.

ELECTROLYTIC Cu REMOVAL FOR ACID RECYCLE

The primary objectives of the laboratory tests for electrolytic removal of Cu and regeneration of HNO_3 at reduced electrolyte temperatures for recycle to the copper strip tank were as follows:

- determine the acid and Cu concentrations that result in the highest current efficiency (CE)
- determine the effect of current density (CD) on CE
- demonstrate the feasibility of a continuous recycle system
- identify acceptable materials of construction for the electrochemical cell
- provide equipment specifications for the recycle system.

Background

The N Reactor fuel billets are copper clad before extrusion in the fuel fabrication process. This cladding is removed by dissolving Cu in HNO_3 according to the reaction in Equation 13. The strip solution is batch discharged and replaced as the Cu concentration approaches 180 g/L (1.5 lb/gal) and the acid concentration reaches 3.0 to 4.5 M HNO_3 (1.6 to 2.4 lb/gal).

As shown in Equation 14, Cu can be recovered as a solid and HNO_3 can be regenerated by electrowinning the solution. Since HNO_3 is the solvent of choice, the electrolytic and chemical reactions compete. Electrolytic removal of Cu can be achieved, however, if the rate of the chemical reaction can be decreased by reducing the electrolyte temperature.

Due to limited available floor space in the plant, high-current-density operation, which requires a smaller cell, was desirable for the electrowinning system. The high concentrations of Cu in the electrolyte made this system amenable to this type of operation. Moreover, earlier studies by Hara and Weakley^(a) indicated that air sparging was necessary to remove excess NO_2 from solution before electrolysis. Air sparging during electrolysis would not only remove NO_2 , it would enhance mass transfer to the cathode in high-current-density operation. Therefore, air sparging was incorporated into the design of the laboratory-scale and pilot-scale systems.

Experimental Procedure

Three types of solution were used in the laboratory studies. Preliminary tests were run with synthetic solutions made from HNO_3 and $\text{Cu}(\text{NO}_3)_2$ crystals as well as from samples of diluted Cu strip solution (tank 10). These samples

(a) F. T. Hara and E. A. Weakley. 1972. Invention Report on Electrolytic Removal of Copper from Nitric Acid.

were collected at the time of tank dumping and, in general, contained about 160 g/L Cu and 4.0 M HNO_3 . For the laboratory-scale continuous system runs, Cu alloy shavings from UNC were dissolved in HNO_3 to simulate the proposed recycle system.

Synthetic solutions were satisfactory to determine the operating ranges, but actual strip tank solution or simulated solution that contained the Si and Mn impurities was used to determine the operating conditions. Operating ranges were found by electrowinning 250 mL of synthetic solution in beakers; reduced temperatures were maintained with a water bath. Further tests were conducted with the diluted strip solution samples in a 2-L plexiglass cell using a stainless steel cathode and a platinum anode. The electrolyte was cooled by circulating it through the tube side of a cooling coil placed in a methanol/water bath. In the continuous system, the composition of the electrolyte was maintained at steady-state conditions by dissolving Cu in a HNO_3 'strip' tank before circulation to a cooling flask, as shown in Figure 2. The cooled electrolyte was then circulated to an air-sparged cell that contained a cooling coil in the bottom; methanol and water were circulated through the tube side. The cathode was a Cu plate made of UNC Cu alloy #655 and the anodes were titanium that was coated with iridium oxide. Anode bags and diaphragms were made of various materials including cotton, polypropylene, and Nafion®, a cation-selective membrane.

FIGURE 2. Laboratory-Scale Electrowinning System for Continuous Recycle

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Copper concentrations were determined by either AA spectroscopy or titration against an NaOH standard. Acid concentrations were determined by titration against the same standard. Some ICP analysis was performed to determine concentrations of minor impurities and to verify the other analytical results.

Results and Discussion

An acid concentration greater than 3.0 M HNO_3 is required to operate the Cu strip tank. However, the acid concentration for which electrowinning can be conducted is limited to less than 6 M HNO_3 and to date only a 2 M HNO_3 solution has been used on a pilot scale (Mockrin et al. 1977). Therefore, preliminary tests were run on solutions containing about 3.0 M and 4.0 M HNO_3 and a range of Cu concentrations to determine the effect of acid concentration, copper concentration, and current density on current efficiency. The results are summarized in Table 7.

Several trends were observed. At high CD, the CE improved as the concentration of Cu increased to about 100 g/L. For the solutions near 3.0 M HNO_3 , the CE appeared to stabilize for Cu concentrations greater than 100 g/L, but for the solutions near 4.0 M HNO_3 , the CE dropped to 0% for Cu concentrations greater than 100 g/L. For all the Cu concentrations, a decrease in CE at higher acid concentrations was generally observed. Furthermore, the CE appeared to improve slightly at higher CD.

A second set of tests was run with actual strip tank solution diluted to 3.0 M and 100 g/L Cu as well as 4.0 M HNO_3 and 120 g/L Cu. The results are summarized in Table 8. These results confirm that a higher CE is achieved at a lower acid concentration. For 3.0 M HNO_3 solutions, an average CE of 65% was observed for CD ranging from 0.13 to 0.25 A/cm^2 and for 4.0 M HNO_3 solutions, an average CE of 42% was observed for CD ranging from 0.13 to 0.26 A/cm^2 . This represents a 35% decrease in CE for a one-molar decrease in acid concentration. In these tests, no clear trend in CE as a function of CD was observed. Also, the CE for the 4.0 M HNO_3 and 120 g/L Cu solution was greater than that observed in the previous tests.

Based on these observations, a continuous system was designed in which the nominal acid and copper concentrations of the electrolyte were 3.0 M and

TABLE 7. Current Efficiency as a Function of Acid Concentration, Cu Concentration, and Current Density at Reduced Temperature of Synthetic Copper Strip Solutions

H, Molarity	Cu, g/L	Temperature, °C	Current Density, A/cm ²	Current Efficiency, %
2.8	45	7	0.22	27
2.7	76	6	"	57
2.8	111	9	"	71
2.9	152	10	"	70

3.8	35	-	0.22	15
4.0	100	9	"	51
3.9	135	8	"	6
3.9	135	9	"	0

2.8	26	5	0.11	19
3.2	76	5	"	56
2.8	91	6	"	67
3.1	145	5	"	56

4.3	12	5	0.11	14
3.9	52	5	"	38
4.0	115	5	"	0
3.9	157	6	"	0

2.8	45	3	0.028	55
2.8	91	3	"	55
2.8	111	4	"	0
3.1	145	5	"	0

100 g/L, respectively; acid and Cu were added to the electrolyte via a strip tank at regular intervals to simulate actual operating conditions. The system was designed to process 0.45 kg (1 lb) of Cu per day (24 h) at a CE of 60%. An electrolyte temperature of less than 15°C and a CD of 0.19 A/cm² was maintained. The results are shown in Table 9.

In Run 1, Cu and makeup acid were added to the strip tank at 10-h intervals; 216 g of Cu were added in 10 h. This same amount of Cu and an increased amount of makeup acid were added at 2-h intervals for Run 2. The excess acid in the second run appeared to decrease the average CE. The unstable CE for

TABLE 8. Current Efficiency as a Function of Acid Concentration and Current Density at Reduced Temperatures of Diluted Cu Strip Solutions

Temperature, °C	Current Density, A/cm ²	Current Efficiency, %
4 <u>M</u> HNO ₃ 120 g/L Cu		
8	0.13	52
9	0.18	31
9	0.20	53
11	0.23	30
10	0.24	31
5	0.26	53
12	0.36	41
11	0.38	47
12	0.39	43
12	0.40	28
3 <u>M</u> HNO ₃ 100 g/L		
12	0.13	72
13	0.13	66
12	0.17	57
13	0.24	65
13	0.24	67
12	0.25	65

TABLE 9. Results of Continuous Electrowinning System

	Run 1	Run 2
Length of run, h	31.45	27.25
Electrolyte, °C	4 to 10	4 to 15
Current efficiency, %		
Average	55	33
Range	39 to 65	26 to 70
Change in H ⁺ in cell, Normality		
Catholyte	3.4 to 3.1	3.5 to 2.8
Anolyte	3.4 to 4.2	3.5 to 4.2
Efficiency of acid regeneration, %	55	--

both runs was due primarily to inadequate process control on all parameters. The feed stream to the cell was not filtered and impurities such as Mn as a permanganate or MnO_2 and Si as silicic acid tended to accumulate in the anode compartment. Based on the results, a pilot-scale system was designed. Details are given in Appendix B.

Cooling the total volume of electrolyte requires a large chiller. Therefore, an alternative scheme was considered for the recycle. Nafion was used as a diaphragm to separate the anolyte from a cooled catholyte and from a catholyte treated with sulfamic acid. Preliminary tests indicated that movement across the membrane was a limiting factor for high-current-density operation and further study was not pursued.

Conclusions

High-current-density electrowinning for Cu removal and HNO_3 regeneration is a technically feasible system based on existing patent information and as demonstrated by the results of PNL laboratory-scale testing. The operating parameters have not been optimized and pilot-scale operation would be imperative. It would appear, however, that a cell operated at about 0.22 A/cm^2 with a solution containing 3.0 M to 4.0 M HNO_3 and 100 g/L Cu maintained at a solution temperature of 5°C could be expected to satisfactorily treat the spent Cu strip acid for recycle. The temperature of the strip tank solution would have to be maintained near 70°C for an adequate rate of Cu dissolution.

ELECTROLYTIC Cu REMOVAL FOR ACID CLEANUP

For acid stream cleanup, Cu can be removed in a usable form from the combined solutions of spent Cu strip acid and Cu rinse water by electrowinning with sulfamic acid (SA) or urea; both of these destroy NO_2 , which catalyzes the competing chemical dissolution reaction. Most of the laboratory tests were run with SA since urea caused undesirable foaming when added to concentrated HNO_3 solutions. Laboratory tests were conducted to determine the cell operating parameters and the composition of the treated stream. A limit of 4.2 g/L Cu could be tolerated in the final effluent.

Experimental Procedure

The same cell and DC power supply used for continuous operation of cooled electrolytes was used for these tests. The cell was a 3.5-L plexiglass cell with one cathode and two anode compartments (see Figure 3). A polypropylene filter media was used as the diaphragm material. An alloy #655 cathode and two iridium-oxide-coated Ti anodes were used. Air was sparged through a series of 1-mm holes in the bottom of the cathode compartment at rate of 2 L/min.

Two Cu-depletion runs were completed: one at 0.22 A/cm^2 and another at 0.11 A/cm^2 . The electrolyte was prepared by combining 2.22 L of UNC tank 10 (Cu strip) solution which had been filtered, 0.73 L of tank 25 (Cu rinse) solution, and 0.55 L water to simulate the average composition of the Cu-bearing waste stream. The initial electrolyte composition was 2.4 M HNO_3 and 126 g/L Cu for the 0.22 A/cm^2 run and 2.8 M HNO_3 and 97 g/L Cu for the 0.11 A/cm^2 . During the runs, SA was added to the catholyte as a solution of 47 g SA to 100 mL H_2O at 60°C when CE began to drop. A ratio of 0.3 g SA to 1 g Cu was maintained. (Additional information on urea and SA addition can be found in

FIGURE 3. Laboratory-Scale Electrowinning Cell

Appendix B.) Periodically, the cathode was removed from the cell and weighed to determine the CE for that time interval. Current density was kept constant as the Cu was removed and the resulting voltage was monitored to determine energy consumption.

Miscellaneous tests were run to determine the effect of other operating parameters. At one acid and Cu concentration, the CD was varied in a 25°C and then a 50°C solution and CE was measured. The effect of air sparging and electrode spacing on the potential and energy consumption were determined.

Results and Discussion

The composition of the Cu-bearing stream before and after electrowinning is listed in Table 10. These compositions are based on the current flow sheet for UNC's fuel fabrication process and the results of the laboratory tests. The concentration of U remained constant for downstream recovery during neutralization. Si was removed by filtration, but Mn remained in solution.

Complete results are presented in graphical form in Figures 4 through 7. The CE for actual combined tanks 10 and 25 waste acid solution containing 4.1 N HNO_3 and 97 g/L Cu stayed nearly constant over the CD range of 0.027 to 0.22 A/cm^2 (25 ASF to 200 ASF) at 25°C or 50°C (Figure 4 and 5). Note that the CE is also a function of Cu concentration and that these tests were run for a constant Cu concentration of 97 g/L. The energy consumption increased from 1.8 to 3.5 kWh/kg Cu with an increased CD. Typically, the energy consumption for Cu electrowinning in a sulfate system ranges from 2.0 to 5.7 kWh/kg Cu with CE of 80% to 90%. The nitrate-SA system compared well with these values.

TABLE 10. Composition of Cu-Bearing Waste Acid Before and After Electrowinning with Sulfamic Acid Addition

Stream	H, Normality	Concentration, g/L					
		Cu	U	Mn	Si	NO_3	SO_4
Feed	3.0	100	1.0	1.0	3.5	--	0
Final	6.4 to 7.0	4	1.0	1.0	0	350 to 380	40 to 80

(a)

(b)

FIGURE 4. (a) Current Efficiency as a Function of Current Density at 25°C with an Electrolyte Containing 4.1 N HNO₃ and 97 g/L Cu; (b) Energy Consumption as a Function of Current Density at the Same Conditions

(a)

(b)

FIGURE 5. (a) Current Efficiency as a Function of Current Density at 50°C with an Electrolyte Containing 4.2 N HNO₃ and 100 g/L Cu; (b) Energy Consumption as a Function of Current Density at the Same Conditions

(a)

(b)

FIGURE 6. (a) Current Efficiency as a Function of Cu₂ Concentration at 17°C and at a Current Density of 0.11 A/cm² (100 ASF) with an Initial Electrolyte Composition of 2.8 N HNO₃ and 97 g/L Cu; (b) Energy Consumption as a Function of Cu Concentration at the Same Conditions

(a)

(b)

FIGURE 7. (a) Current Efficiency as a Function of Cu Concentration at 17°C and at a Current Density of 0.22 A/cm² (200 ASF) with an Initial Electrolyte Composition of 2.4 N HNO₃ and 126 g/L Cu; (b) Energy Consumption as a Function of Cu Concentration at the Same Conditions

With an electrolyte temperature of 40°C, a dense Cu plate was produced with a CE of 95% for electrolytes containing 4.1 to 4.6 N and 90 g/L Cu (Table 11). The energy consumption was 2.4 kWh/kg Cu; the energy consumption tended to increase at 17°C due to increased solution resistance at the lower temperatures. At 60°C, the rate of the chemical dissolution reaction increased and reduced the apparent CE.

As the Cu concentration was decreased, the CE also decreased (Figures 6 and 7). At 0.22 A/cm², the CE dropped from 80% at 126 g/L Cu to 8% at 1.5 g/L Cu. Correspondingly, the acid concentration increased from 2.4 N to 6.4 N. At 0.11 A/cm², the CE dropped from 90% at 97 g/L Cu to 20% at 4 g/L Cu with an acid concentration increase of 2.8 N to 7.1 N.

The electrolyte was air sparged during electrowinning at an air flow rate of 2.2 L/min with one exception; during the 0.22 A/cm² run, the air flow rate was increased as the Cu concentration dropped below 8 g/L in an attempt to improve CE. The results were not conclusive. The potential drop increased as the air flow rate increased (see Appendix B). Subsequently, the energy consumption will increase with increased sparging rates; the optimal sparging rate must yet be determined.

TABLE 11. Effect of Temperature on Current Efficiency and Energy Consumption at 0.11 A/cm² (100 ASF)

Temperature, °C	Current Efficiency, %	Current Efficiency Error, ± %	Energy Consumption, kWh/kg Cu
17	86	3	3.1
42	95	0	2.4
60	83	3	2.6
60	89	7	2.4

Conclusions

The following conclusions can be made based on the laboratory results to date:

- 1) Electrolytic recovery of copper, with sulfamic acid addition, from the waste stream comprising tanks 10 and 25 solutions is technically feasible. The Cu concentration can be reduced to 4 g/L. In addition, the U stays in solution for recovery during neutralization. If the electrolyte is filtered before electrowinning, all the Si can be removed and MnO_2 does not form.
- 2) Laboratory-scale tests indicated that a filtered solution containing 3 N HNO_3 and 100 g/L Cu can be efficiently electrowon at 40°C to an endpoint of about 7 N HNO_3 and 4 g/L Cu. Sulfamic acid (SA) must be added as a hot (60°C) aqueous solution at a ratio of 0.2 g SA to 1 g Cu, which must be maintained throughout the electrowinning process. An air sparge rate of at least 2 L/min is required. At a current density of 0.11 A/cm², the cathodes would be replaced every 10 days if Cu was removed at a rate of 91 kg/day. Each cathode would have 84 kg of Cu deposited on it.
- 3) The operating current density will be chosen on the basis of energy consumption and space requirements, not current efficiency, since the current efficiency remains constant over a large range of current density for a given solution composition.
- 4) The energy efficiency of the cell must be optimized at a chosen current density and electrolyte temperature as a function of the rate of air sparging, the choice of electrode materials, electrode spacing, and hydrodynamics. More work needs to be done in these areas.

- 5) Further studies on plate quality, blank preparation, plate stripping versus cathode casting, and recycle versus disposal of the Cu plate will be needed to determine the labor requirements and process steps auxiliary to the electrowinning system.
- 6) The volume of the Cu-bearing waste stream will be reduced 15% or more during electrolysis. The volume loss will be regained, however, by the increased amount of hydroxide needed to neutralize the regenerated acid if this stream is directly disposed of. However, the effluent may be suitable for recycle to the chemical milling solution, which contains both HNO_3 and H_2SO_4 . The sulfate ion would not be detrimental to the chemical milling bath as it would be to the Cu strip solution. This recycle scheme could reduce the volume of effluent and enhance the recovery of U, because it would be concentrated before precipitation to a diuranate.

METHODS FOR NITRATE RECLAMATION

Three methods for nitrate recovery were proposed and investigated. First, waste HNO_3 and HF-HNO_3 that could no longer be recycled due to high concentrations of minor impurities could be separated from the impurities and recycled by distillation with H_2SO_4 . Second, the cleaned waste acid stream could be neutralized with NH_4OH to recover U as an ammonium diuranate precipitate. The resulting supernate could then be used as a nitrogen fertilizer. The third method involves acid purification by resin bed exchange for separating the acids from metals and salts.

DISTILLATION

Distillation is a method for NO_3 recovery that can reduce the quantity of nitrate discharged to the environment (Dietrich 1973). Recycle methods such as Zr and Cu precipitation can lengthen the usable life of acids, but at some point the minor impurities will exceed maximum limits and spent acid will be discharged after removal of major impurities. Before neutralization, nitric acid can be reclaimed by distillation with sulfuric acid. Normally, HNO_3 remains in the bottoms when an aqueous HNO_3 solution is distilled, but sulfuric acid acts as a water binder to allow the HNO_3 to move to the overhead stream. In this system, minor impurities from the treated stream as well as U remain in the still bottoms with the H_2SO_4 and are removed during neutralization as a sodium precipitate. The pure HNO_3 vapor is fed into a packed column for concentration and recycle to the process. The purpose of the preliminary laboratory test was to determine the concentration of nitric and sulfuric acid in the overhead stream.

Background

Aqueous nitric acid forms an azeotrope at 68.5% HNO_3 . However, if sulfuric acid is added, nitric acid can be concentrated up to 90% (Miles 1961). In industry, a mixture of about 50% to 60% H_2SO_4 and aqueous HNO_3 is distilled to produce a concentrated HNO_3 in the overhead vapor stream.

Nitric acid can be produced from a NaNO_3 waste solution by adding H_2SO_4 ; the reaction is shown in Equation 15. The reaction is usually carried out with

an NaNO_3 to H_2SO_4 ratio of 85:80 to ensure production of NaHSO_4 rather than NaSO_4 (as shown in Equation 16) because sodium bisulfate is easier to remove from the still.

Experimental Procedure

Three spent acid streams were mixed with H_2SO_4 and distilled in simple distillation units. Two samples of Cu strip solution containing 4.0 M HNO_3 and 160 g/L Cu were used. In Run 1, 32 g of 96% H_2SO_4 were added to 125 mL of the copper strip solution; all the NO_3 in the metal nitrates could be displaced by SO_4 . In Run 2, 360 g of 96% H_2SO_4 were added to 125 mL of the same solution, representing about 60% H_2SO_4 in the still bottoms. Upon addition of the H_2SO_4 in Run 2, CuSO_4 precipitated; 125 mL of the supernate was decanted off and used in the still. Distillate fractions were sampled and analyzed for total acid concentration and SO_4 concentration.

Two samples of sodium nitrate wastes were also used. In Run 3, 150 mL of the neutralized supernate was mixed with 68 g of 96% H_2SO_4 , representing a 85:80 ratio of NaNO_3 to H_2SO_4 . In Run 4, the same procedure was used with the mixed slurry. Distillation fractions were sampled and analyzed as before. For all of these runs, laboratory glassware was used and the distillate temperature was monitored.

Two runs were also made with HF- HNO_3 solution containing 0.7 M HF, 6.7 M HNO_3 , and 37 g/L Zr. In Run 5, Zr was first precipitated from the solution and then 75 mL of 96% H_2SO_4 was added to 75 mL of HF- HNO_3 solution. In Run 6, the Zr was not removed before the H_2SO_4 addition. A Teflon® still was used for all HF- HNO_3 distillation. Distillate temperature could not be measured with this apparatus, but distillate fractions were sampled as before.

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A fourth sample of spent acids was also distilled. This waste acid from the U-bearing stream already contained H_2SO_4 , and no additional H_2SO_4 was required. The distillate temperature was monitored and distillate fractions were sampled as before.

Results and Discussion

Acid concentration in the cumulative distillate fraction for the seven runs is shown graphically in Figures 8 through 11. In Run 1, brown gas was observed, indicating some decomposition of HNO_3 at the beginning and end of the distillation. The run was terminated when bumping caused by precipitation of CuSO_4 occurred in the still pot. Concentration of nitric acid in the distillate increased as distillation continued (Figure 8a). After 42% of the solution had been distilled, less than 0.3 g/L H_2SO_4 was found in the distillate. In Run 2, the distillate was yellow, indicating HNO_3 decomposition. The cumulative acid concentration in the distillate dropped as operation continued (Figure 8b). A material balance indicated that essentially all the HNO_3 had been removed after 15% of the bottoms solution was distilled; a total acid concentration in the overhead stream of 16.6 M was measured. Further distillation introduced water and some sulfuric acid to the overhead stream, reducing the cumulative concentration of the distillate to 7.3 M after 35% of the solution had been distilled. Only 0.9 g/L NO_3 remained in the bottoms stream at the end of the run.

For NaNO_3 distillations, differences in the distillate compositions for the two runs were not observed. Results were combined on the graph in Figure 9. Concentration of nitric acid in the cumulative distillate increased as distillation continued. In Run 3, 80% of the NO_3 was removed from the bottoms after 69% of the bottoms was distilled. In Run 4, 72% of the NO_3 was in the overhead stream after 67% of the bottoms had been distilled. Some SO_4 was found in both distillates as 70% of the bottoms was distilled. The bottoms product solidified quickly as the still pot cooled after a run and was difficult to remove without reheating.

Results for the HF-HNO_3 distillation were similar for both runs, indicating that the presence of Zr had little effect on the distillate composition (Figure 10). The cumulative distillate concentration followed the same trend

FIGURE 8. Concentration of Free Acid in Distillate from the Copper Strip Solution (tank 10): (a) initial bottoms contained enough H_2SO_4 to replace the NO_3 in the metallic salts; (b) excess H_2SO_4 was added, resulting in an initial bottoms composition of 60% H_2SO_4 and 40% aqueous HNO_3 .

FIGURE 9. Concentration of Free Acid in the Distillate from Conversion of NaNO_3 to HNO_3 with H_2SO_4

FIGURE 10. Concentration of Free Acid in the Distillate from the HF-HNO₃ Solution with an Initial Bottoms Composition of 60% H₂SO₄

as that observed for the Cu strip solution combined with H₂SO₄ at 60%. Most of the HNO₃ distilled over as 13% of the bottoms was distilled. As operation continued, water and SO₄ were found in the distillate which accounts for the drop in acid concentration.

For distillation of the U-bearing solution containing about 2.6 N H₂SO₄ and 3.0 N HNO₃ initially, the concentration in the distillate increased until 60% of the initial bottoms volume was distilled (Figure 11). At that point, about 80% of the HNO₃ had been recovered in the distillate. Further distillation produced fractions richer in H₂O than HNO₃. When 75% of the initial bottoms volume was distilled, nearly 100% of the HNO₃ was recovered.

FIGURE 11. Concentration of Free Acid in the Distillate Fractions from the U-Bearing Solution Containing 2.6 N H₂SO₄ and 3.0 N HNO₃

Conclusions

The following conclusions were derived from the results of the preliminary distillation tests:

- 1) If 60% of the initial bottoms solution is H_2SO_4 , the initial distillate fractions are concentrated nitric acid, which does not need to be further concentrated in a column. However, the concentration of residual NO_3 in the bottom stream is not known at this time.
- 2) For conversion of NaNO_3 to HNO_3 , the distillate concentration increased as operation continued, but the concentration was too low for recycle without rectification.
- 3) When H_2SO_4 was added to the Cu strip solution in quantities great enough to convert the metal nitrates to metal sulfates with no excess H_2SO_4 present, the acid concentration of the resulting distillate was too low; rectification would be required. Some problems may also be encountered as the insoluble metal sulfates form on the still pot.
- 4) Nearly 100% of the HNO_3 was recovered from the U-bearing solution without additional H_2SO_4 . The resulting distillate would require concentration to 57% before recycle.
- 5) Although some HNO_3 decomposition was observed, it did not appear to be extensive.
- 6) Very low concentrations of SO_4 were found in the distillate, suggesting that this parameter can be controlled for extended acid life. It is not known what concentration of SO_4 can be tolerated within the individual process solutions.
- 7) Only a few of the final still bottoms were sampled and analyzed for NO_3 . For those measured, the NO_3 concentration was low, but future work needs to focus on this parameter.

NITROGEN FERTILIZER PRODUCTION

In conjunction with the DOE By-Product Utilization Program, a method for the reclamation of nitrates as nitrogen fertilizer was proposed as an alternative chemical waste system. This system would consist of several process steps already discussed. Zr-bearing solutions and a Cu strip solution would be rejuvenated by precipitating Zr and Cu, respectively; this acid would be recycled until the concentration of minor impurities exceeded acceptable limits. Spent acid would then be neutralized with ammonium hydroxide to recover uranium as ammonium diuranate and to produce an ammonium nitrate/sulfate supernate. After separation and treatment to remove residual metals and radionuclides, the supernate could be used as a nitrogen fertilizer. Approximately 121,000 GPY of ammonium nitrate/sulfate solution containing 8% N and 4% S would be produced.

During the U conversion process, Kerr-McGee Nuclear Corporation (KMNC) currently produces an ammonium nitrate solution which is used as a nitrogen fertilizer at the Sequoyah, Oklahoma, facility. In this process, uranium oxide is dissolved in nitric acid and then is separated from the impurities in a solvent extraction step. The resulting raffinate contains about 6% nitric acid and low concentrations of U, Ra, and other heavy metals. The raffinate is neutralized with ammonia in a four-basin clarifier. A soluble barium salt is then added to the neutralized raffinate to coprecipitate Ba-Ra sulfate. The Ra concentration and the pH of the treated raffinate is measured before it is stored in holding ponds for later use. The composition of a typical sample of neutralized raffinate is shown in Table 12. For comparison, the composition of the present UNC supernate resulting from NaOH neutralization is also shown.

As part of the operating license agreement with the U.S. Nuclear Regulatory Commission (NRC),^(a) KMNC has been producing nitrogen fertilizer for use at their facility since 1973. KMNC holds a state license as a fertilizer manufacturer as well. After the initial environmental impact statement was completed, a testing program for land application was initiated in 1973 and is currently ongoing. The objective has been to assess the impact of the

(a) Title 10, Code of Federal Regulations, Part 40. Source Material License No.-SUB 1010, Amendments Nos. 1, 2, 4, 5, 11, 12, 13, 15, 17, 18, 20, 26.

TABLE 12. Composition of Raffinate Fertilizer and of Current
UNC Sodium Nitrate Supernate

Component	Raffinate Fertilizer, mg/L	UNC Sodium Waste, mg/L
Al	3.1	<0.03
As	2.0	<0.02
B	1.6	<0.02
Ba	0.49	<0.002
Cd	<0.070	<0.005
Co	0.31	--
Cr	<0.26	5.6
Cu	5.4	<0.005
Fe	<0.24	<0.005
Hg	<0.005	--
K	--	14
Mg	170	<0.1
Mn	3.0	<0.005
Mo	16	<0.01
Na	--	38,000
Ni	8.3	<0.02
P	--	10
Pb	0.80	<0.05
S	--	4,000
Se	1.0	<0.2
Si	--	5
Sn	0.18	630
Ti	<0.17	<0.005
V	0.23	<0.005
Zn	1.9	<0.005
F	46	?
W	2.2	--
Be	<0.010	<0.002
Li	1.1	<0.005
Tc-99	--	0.073(a)
U	0.04	<0.5
	<u>pCi/L</u>	<u>pCi/L</u>
Alpha	200	?
Ra-226	0.17	--
Th-230	0.036	--
Th-232	0.009	--
Beta	--	1,200,000

(a) Estimated.

fertilizer and to input data for a continuous fertilizer management program. Between 1973 and 1976, small plots of pastureland were used to compare the effectiveness of the raffinate and commercial nitrogen fertilizer on the foliage. The accumulation of heavy metals and radionuclides in the soil, water, and plants was monitored. It was concluded that raffinate fertilizer gave similar foliage production, forage quality, and nitrogen recoveries to those of commercial ammonium nitrate fertilizers (Shelley 1979).

The testing program began to expand in 1977. A 160-acre site was prepared that year; the area had surface run-off water control, ground and surface water monitoring systems, tensiometers and soil sorption cups, and vegetation and soil sampling locations. Five provinces of timberland and grassland vegetation types were established. Since that time, additional land has been similarly prepared for a current total of 3005 acres. Fertilizer application rates have ranged from 450 kg N/ha to 1680 kg N/ha on vegetation such as native grasses, timber, and forage crops. Each spring an agronomist at Oklahoma State University visits the site and determines application rates for the upcoming growing season. The $\text{NO}_3\text{-N}$ concentration in the soil profile is monitored throughout the year to determine whether these rates need to be modified.

In 1979, twenty head of cattle were acquired. Half of the herd was grazed on forage fertilized with the raffinate fertilizer to determine the effects, if any, within the food chain. No ill effects were observed, as confirmed by the Oklahoma State University Animal Disease Diagnostic Laboratory, U.S. Agricultural officials, and the NRC. Currently, 392 head of cattle graze on raffinate-fertilized pastures.

During the last 10 years, no increase in radioactivity or heavy metal concentration in the soil, water, foliage, or animal tissues has occurred. The amount of available nitrogen has increased significantly; therefore, it was concluded that the treated raffinate was very similar to commercial nitrogen fertilizers. Application for an amendment to the operating license was made to NRC for use of the fertilizer on an unlimited basis.

As a result, fertilizer can be sold for offsite use, but KMNC is responsible for analyzing the resulting forage. The cost of forage analysis plus the expense of shipping large quantities of solution containing only 3% to 6%

nitrate has made this option economically unattractive when compared to alternative disposal methods such as deep-well injection. Therefore, KMNC is currently using part of the fertilizer on site for the production of forage and seeds which are then sold off site after appropriate analysis. The remaining solution is injected into deep wells.

Although KMNC has set a precedent using ammonium nitrate solutions as a fertilizer by-product, the UNC fertilizer will differ in composition from the KMNC raffinate fertilizer, and field tests to determine application rates would be required. The UNC fertilizer has a higher nitrate concentration than the KMNC fertilizer and contains beneficial sulfates. The composition is similar to locally produced commercial fertilizer for use on such crops as potatoes. The ammoniacal solution will contain Tc-99, which must be removed by precipitation or anion exchange before release as a fertilizer. Cu, Cr, and U are likely to be present in concentrations higher than those shown in Table 12 for the ammonia system. Final cleanup could be accomplished, however, with a chelating bed to reduce cation concentrations to acceptable levels.

There are several advantages to producing fertilizer as a by-product from spent acids. First, production of useful by-products from the nuclear industry is in keeping with the by-product utilization plan. With this process, nitrates are reclaimed as fertilizer, and if it is found to be economically feasible, Zr can be reclaimed as a fluozirconate. Second, nitrates are released to the environment in a usable form and at a controlled rate. Third, the volume of liquid waste going to burial is significantly reduced. Fourth, ammonium diuranate is a purer product than Na diuranate and ammonium hydroxide is a less expensive neutralizing agent than NaOH. Finally, proposed process steps such as Zr precipitation with NaF, U precipitation with ammonium hydroxide, Tc-99 removal with anion exchange, and cation removal with a chelating bed are based on existing technology and commercially available equipment would be used.

ACID PURIFICATION BY RESIN BED EXCHANGE^(a)

Acid purification, a process similar to ion exchange, has been identified as a method for separating acids from metals and salts. It could be used to rejuvenate spent HNO_3 from the Cu strip solution. In this process, a resin with greater affinity for acid than for metals is used. As the spent solution contacts the resin, the acids are retained on the resin while the metallic ions are allowed to pass through. The sorbed acid is subsequently recovered by backwashing with water.

The Acid Purification Unit (APU®), a commercial acid purification system, was used for tests with the Cu strip solution. It is shown in Figure 12. The resin bed sits in the center with an acid and water reservoir on each side. The flow of water and acid is alternated through the resin by level indicators. Three stainless steel sensing electrodes in each reservoir determine the solution level. Correspondingly, the solution level in each reservoir controls the flow valves and air pressure to the system, allowing the APU to cycle continuously with minimal operator attention.

Experimental Procedure

An experimental investigation was carried out using spent tank 10 solution. It was necessary to filter the solution through a 76-cm-long, 20-micron filter to remove the gelatinous silicic acid. This material immediately clogged a small-capacity, 25-micron filter on the system inlet. Colloidal material that was allowed to pass into the system would have collected in, and fouled, the resin. Use of a commercial centrifuge system to remove the colloidal or gelatinous material was also investigated. The unit readily removed precipitated solids, but the density difference was insufficient for substantial removal of the silicic acid.

The initial setup of the APU is crucial. The length of each step is determined by the electrode's height in the reservoir. Heights are adjusted to optimize product (purified acid) and by-product (Cu solution) concentrations. The initial settings tested were those recommended by Eco-Tec to effect Cu

(a) This section was written by L. A. Sigalla and R. P. Allen.

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Results and Discussion

In Table 13, representative results are presented from the final series of tests. Samples from some of the intermediate cycle points are included to illustrate concentration changes over time during the process cycle.

The results show that Cu removal can be achieved with minimal loss of acid. A mass balance based on the relative volumes of the feed, product, and by-product steps indicates the removal of about 30% of the Cu and the loss of about 1% of the acid in the feed, and reflects the high affinity of the resin for nitric acid and the relatively high Cu levels in the feed. Operating the system on a continuous basis to maintain a lower Cu concentration would probably result in less efficient Cu removal. However, increasing the system capacity would compensate for this. The increased concentration of acid over the feed levels should also be noted; this result is typical for nitric acid operations.

Copper concentration in the recycle stream is a function of resin bed size. The present 15.2-cm APU processes about 3.8 L of feed per 13 min cycle, or about 416 L/day for continuous operation. This corresponds to the removal of about 22.7 kg of Cu and the loss of about 1.8 kg of acid per day. The process can be scaled up by increasing the resin column diameter to give four times the capacity for a 30.5-cm column, or seven times the capacity for a 40.6-cm column.

TABLE 13. Results for APU Tests with Cu Strip Solution

<u>Sample</u>	<u>Cu, g/L</u>	<u>% Cu</u>	<u>Acid, g/L</u>	<u>% Acid</u>
Initial feed	180	100	264	100
Product				
15%	156	90	228	90
45%	144	80	252	95
75%	96	50	324	120
Total	120	65	288	110
By-product				
20%	12	10	2	1
55%	48	30	5	2
90%	168	95	8	3
Total	72	40	5	2

Conclusions

Satisfactory separation methods must be found to remove gelatinous silicic acid from the Cu strip solution before treatment. If this problem can be resolved, the APU appears to be a promising technique for acid rejuvenation.

METHODS FOR DENITRIFICATION

Three methods were reviewed for denitrification of the nitrate waste. First, dried nitrate waste can be thermally decomposed by high temperatures (greater than 500°C) into N_2 , O_2 and NO_x gases. NO_x releases can be avoided by keeping the temperature over about 2000°C. The second method involves chemical destruction of aqueous nitrate waste at or near ambient temperatures. The third method involves biodenitrification.

THERMAL DECOMPOSITION

A high-temperature fluid wall (HTFW) reactor has been evaluated by Rockwell personnel at Rocky Flats and tested by Thagard Research (Johnson et al. 1982; Meile et al. 1984a, 1984b). The HTFW reactor is capable of rapidly heating dried nitrate salt with carbon additions to about 2200°C. This produces low NO_x in the out gas and reduces the NO_3^- in the waste by ~96%. Various additives were tested to enhance nitrate destruction and to reduce NO_x release. This HTFW process is still experimental and the equipment cost of a small 15-cm unit is over \$500,000. A larger-scale reactor (30 cm) has been set up at Rocky Flats and is expected to reduce NO_3^- by 94% to 99.7% (Arnold and Johnson 1984), but no data are currently available.

An alternative technique using a plasma arc process is also being investigated at Rocky Flats (Arnold and Johnson 1984). Tests are currently being conducted at Westinghouse, Pittsburgh, in a plasma arc reactor. Very high temperatures (~2000°C) are produced by a plasma arc and should result in complete NO_3^- destruction. No results have been reported to date.

CHEMICAL DESTRUCTION

Rockwell personnel at Rocky Flats have tested a molten salt reactor (MSR) for converting the NO_3^- wastes to N_2 gas and CO_2 using coke in a molten $NaCO_3$ bath (875 to 1050°C) (Meile et al. 1984a). Although the NO_3^- reduction was found to be very good (~99%) and the NO_x gas generation was below 500 ppm, there were considerable feed and hardware problems with the MSR; therefore, this method appears unfeasible at the present time.

Reducing nitrate wastes in an aqueous solution with various reducing agents, reaction promoters, and catalysts is being tested at Rocky Flats (Meile et al. 1984b; Arnold and Johnson 1984). The best reducing agent tested for destruction of NaNO_3 and HNO_3 was found to be formic acid. The greatest nitrate destruction was 96%, which was obtained in a two-step process: adding H_2SO_4 to the waste and distilling off the resultant HNO_3 , then refluxing the HNO_3 for 3 h with formic acid. If the HNO_3 is not distilled out of the H_2SO_4 mix, a nickel catalyst is required to obtain high destruction yields; however, a high NO_x gas concentration (4400 ppm) was obtained in the off gas and is a potential problem.

In addition to formic acid, other reducing agents tested include urea, formaldehyde, sulfamic acid, sucrose, hydrogen peroxide, and ferrous sulfamate. Reaction promoters tested were H_2SO_4 , H_3PO_4 , and KHSO_4 .

The two-step nitrate destruction process is potentially a viable method for reducing the nitrate content of the waste if no use is found for reclaimed acid. Greater than 90% denitrification of aqueous waste can be expected. NO_x release is a potential problem with this process and warrants further investigation.

BIODENITRIFICATION

Anaerobic soil bacteria have been used to destroy the nitrates in solvent extraction wastes generated at the ORNL Y12 plant (Clark et al. 1975a; Napier 1976; Holland 1980). This waste contains up to 39% nitrates, including Al nitrate, with about 4% free acid. Impurities include F, Cl, and heavy metals. Four unlined 1-acre ponds of acid waste must be denitrified as well. The pond wastes contain heavy metal and 1% to 9% nitrate. The average pH is 1.5 with approximately 4% to 12% free acid.

Process Description

ORNL has operated two 25,000-gal stirred-bed reactors continuously since 1976 with only one shutdown to remove the solids for use as biomass in the pond denitrification. The raffinate waste is added at an adjustable rate that is dependent on the nitrate concentrations. At 39% nitrate, the solution is added

at a rate of 0.5 gpm per reactor. Calcium acetate is added as a carbon source at a ratio of 1.1 to 1.3 C to N by weight. The acid stream is not preneutralized because enough Ca carbonate and Al hydroxide is formed during the process to neutralize the acid and form a slurry of 5% solids.

The bacteria convert C and NO_3 to CO_2 , H_2O , and N_2 . The bacteria grow at a pH of 6.8 to 10, but tend to buffer themselves to a pH of 7 to 7.2. About 1000 lb of nitrate per day per reactor is denitrified. The residence time in the reactor is 25 days. Once a day a volume of denitrified solution equal to the volume of the daily input is withdrawn. Pond S3 was converted to a large stirred-bed reactor by installing pumps to circulate the solution below the pond surface (Napier et al. 1984). Ca carbonate, $\text{Ca}(\text{OH})_2$, lime, and sludge from the bioreactor were used to adjust the pH to 7.0 to 7.2. Acetic acid was added as a carbon source at the ratio of 1.1 to 1.3 C to N by weight. The pond was inoculated with the anaerobic bacteria. In one pond, the initial nitrate concentration was 8800 ppm; nitrate was decomposed at a rate of 300 ppm/day to acceptable nitrate levels of 2 ppm in 21 days. The process was slower than anticipated due to low phosphate concentration, which must be maintained between 2 and 40 ppm. Typical pond composition is shown in Table 14.

Capital and Operating Costs

In 1976, the acid recovery and biodenitrification facility cost \$1700K. The operating costs are competitive with other methods of nitrate destruction. The ratio of evaporator:crystallizer:bioreactor operating costs for the stirred-bed reactor was 1:2.1:4.3 on a cost-per-gallon basis. Denitrification of the ponds is less expensive. The 9.5×10^6 L pond containing 8800 ppm was denitrified at a cost of \$125K. The carbon source is the largest contributor to the operating cost of the bioreactor and the pond. Another large cost was water analysis. Labor would be inexpensive for the bioreactor since it requires only one operator and virtually no labor is required for the ponds. Today the ponds are being replaced by 500,000-gal storage tanks which will be stirred, neutralized, and inoculated for biodenitrification.

TABLE 14. Composition of the Denitrified Pond at ORNL Y12 Facility

Compound	Composition, ppm				State Regs
	Before Treatment	After Neutralization	After Biodenitrification ^(a)	^(b) BAT	
Cd	0.2	0.02	<0.0036	0.26	0.01
Cr	5.4	0.005	<0.012	1.71	0.05
Cu	5.1	0.019	0.048 to 0.18	2.07	0.02
Pb	0.89	<0.1	<0.06	0.43	1.0
Ag	<0.001	<0.006	<0.007	0.38	0.05
Zn	4.2	<0.002	0.037 to 0.73	1.48	0.3
Be	0.04	<0.001	<0.0001	0.13	0.01
Hg	--	--	<0.001	0.001	--
Se	--	--	<0.02	1.8	0.02
Ni	41.0	0.15	<0.012 to 0.35	2.38	2.38
CN	--	--	<0.09 to 0.18	0.65	0.1
NO ₃	--	--	<10	20	90
TSS ^(c)	--	--	33 to 42	30	20
COD ^(d)	--	--	56 to 112	30	20
pH	2.0	--	7 to 7.5	6 to 9	6 to 9

(a) Average of 9 samples from 4 ponds.

(b) Best available technology.

(c) Total suspended solids.

(d) Chemical oxygen demand.

300 AREA SOLAR EVAPORATION BASIN

Use of a solar evaporation basin located in the 300 Area of the Hanford Site was considered as an interim measure to reduce the volume of liquid wastes sent to the 183-H basins. These ponds could also be integrated into proposed long-term disposal plans.

Regulatory Requirements

A review was made of state and federal regulations pertaining to construction and operation of the proposed solar evaporation pond. It was found that the pond would have to meet the Resource Conservation Recovery Act (RCRA) standards. These standards require a minimum of one impermeable synthetic liner with a ground water monitoring program. Alternatively, a double-lined pond with a leachate detection and collection system can be used. If this option is exercised, ground water monitoring is not required.

The state regulations (WAC 173-303 [May 17, 1984]) are essentially the same as those outlined by RCRA. However, the state has two different classifications of waste: dangerous and extremely hazardous. The requirements for dangerous waste are the same as for RCRA (e.g., single liner with ground water monitoring); the extremely hazardous waste must have a double liner system. The process of classifying the waste as dangerous or extremely hazardous is fairly involved and not yet clearly defined. Subsequently, the cost of building a pond becomes prohibitive with the contingency necessary to cover the unknown requirements; further investigation will not be pursued.

ALTERNATIVE DISPOSAL METHODS

Alternative methods for disposing of nitrate waste were reviewed. Included in the study were laboratory-scale grout tests and a review of impoundment requirements.

PRELIMINARY GROUT TESTS^(a)

Background

A Transportable Grout Facility (TGF) is being planned to solidify selected low-level liquid wastes at Hanford using cementitious grouts. The resulting grouts will be pumped to open trenches or vaults for final disposal. Operation of the facility with Hanford facilities waste (HFW) is scheduled for 1986. The liquid waste is a mixed phosphate/sulfate solution resulting from decontamination operations of N Reactor and ion exchange regeneration. ORNL is providing preliminary grout formulations for the initial operation of the TGF. The Hanford Grout Technology Program at PNL is responsible for verifying that the grout formulations can be safely and reliably processed and that the grouts that are produced provide an adequate degree of public safety.

Grouting may also be an alternative in the disposal of UNC fuel processing wastes. These liquid wastes may either be mixed with other liquid wastes at Hanford or may serve as a single feed for the TGF. A small scoping study was conducted to identify the properties of grouts produced with such a waste. Emphasis was placed on the rheological properties and formulation criteria adopted for the TGF. The specific criteria that were addressed are summarized below:

- The rheological properties of the grout formulations shall be tailored to be compatible with the safe and reliable operation of the current reference process.

(a) This section was written by R. O. Lokken.

- The grouts shall harden to a minimum compressive strength of 50 psi within 28 days of completing the emplacement of grout.
- No free-standing liquid shall exist on the surface of grouts 28 days after completing the emplacement of grout.

The current process specifies a nominal grout flow rate of 50 gal/min through a 2-in.-diameter pipe. Rheological property measurements of the grouts are necessary to ensure that the grouts can be effectively transported from the mixer to their ultimate destination. The grouts must be pumped in the turbulent flow regime to minimize particle segregation and excessive buildup on the inside pipe walls. This criterion is satisfied when a Reynolds number greater than 2100 is determined.

The flow properties of grouts are classified as non-Newtonian, usually described as Bingham plastics or power-law fluids. Non-Newtonian fluids do not exhibit a direct proportionality between pressure loss and flow rate at a constant temperature and pressure. The power-law model is based on the assumption that the fluid exhibits a proportionality between the logarithm of pressure loss and the logarithm of flow rate, with a starting stress in the region of laminar flow, and represented by the equation (Smith 1976):

$$S_s = K'(S_r)^{n'}$$

where S_s = shear stress, Pa

K' = intercept of lines (fluid consistency index), $\text{lb}_f\text{sec}^{n'}/\text{ft}^2$

S_r = shear rate, sec^{-1}

n' = slope of the shear-stress/shear-rate curve (flow behavior index), dimensionless.

These two parameters are used in the calculation of Reynolds number by:

$$N_{Re} = \frac{1.86v^{(2-n')}\rho}{k'(96/d)^{n'}}$$

where N_{Re} = Reynolds number, dimensionless

v = slurry velocity, ft/sec

ρ = slurry density, lb/gal

d = inside pipe diameter, in.

Frictional pressure drop is calculated by:

$$\Delta P_f = \frac{0.39 \rho v^2 f}{d}$$

where P_f = frictional pressure drop, psi

L = length of pipe, ft

f = Fanning friction factor, dimensionless.

The Fanning friction factor is related to Reynolds number by $16/N_{Re}$ in the laminar flow region and approximated by $0.0175 N_{Re}^{(-0.123)}$. The frictional pressure drop calculation is used as an aid in equipment design.

Experimental Procedure

The grouts in this study were produced with a dry-solids blend that was a preliminary ORNL recommendation as the reference for HFW. The blend consisted of 40 wt% types I & II Portland cement, 48 wt% Class F fly ash, and 12 wt% Attapulgit 150 clay. The oxide composition and physical properties of these materials are given in Tables 15 and 16, respectively.

The waste was received from UNC on May 31, 1984, and was labeled "Waste #766, 183-H." The waste consisted of a yellowish supernate and a dark precipitate; the solids comprised approximately 32.4 vol% of the total waste. The pH of the filtered supernate was 12.94 and the density of the composite waste was 1.24 g/cm^3 . The chemical composition of the supernate is shown in Table 17.

A series of grouts were prepared with the composite waste and with supernate alone, using mix ratios from 960 to 1080 g of dry solids per liter of waste. The dry blends were blended in a twin-shell V-blender for 23 h.

TABLE 15. Oxide Composition of Dry Solids, wt%

<u>Oxide</u>	<u>Portland I & II Cement</u>	<u>Attapulgit</u>	<u>Fly Ash</u>
Al ₂ O ₃	3.40	8.70	23.10
B ₂ O ₃			0.44
BaO	0.10	0.02	0.17
CaO	63.00	5.30	8.60
Fe ₂ O ₃	5.10	2.80	5.00
K ₂ O	0.40	0.80	0.70
MgO	1.00	9.00	1.95
Na ₂ O	0.19		3.10
P ₂ O ₅	0.10	0.80	0.70
SO ₄	3.30		0.71
SiO ₂	23.00	53.00	45.00
SrO	0.05		0.26
TiO ₂	0.20	0.37	3.40
ZnO	0.03	0.09	0.03
Total	99.86	80.88	93.16

TABLE 16. Densities and Surface Areas of Dry Solids

	<u>Cement</u>	<u>Fly Ash</u>	<u>Attapulgit</u>
True density, g/cm ³	3.20	2.29	2.50
Bulk density, g/cm ³	1.60	1.58	0.67
BET surface area, m ² /g	1.07	0.71	20.20
Blaine fineness, cm ² /g	3880	2950	ND ^(a)

(a) ND = not determined.

for 23 h. In all cases, grouts were prepared using 1 L of waste solution. The waste was added to a Hobart mixer before the solids addition. The grouts were mixed for 3 min at the low speed of the mixer using a wire whip. The rheological properties of the grouts were measured with a Model RV100 Rotovisco viscometer using the manual mode. Shear stress was determined at 10% increments in

TABLE 17. Chemical Analyses of Waste #677 Supernate

<u>Component</u>	<u>g/L</u>
B	0.004
Cr	0.005
K	0.014
Na	88.1
P	0.01
Si	0.005
Sn	0.063
F	5.0
NO ₂	0.40
NO ₃	195
SO ₄	11.5

shear rate up to 1170/s, and again from 1170/s with decreasing increments following 5 min at the maximum shear rate. In addition to the rheological property measurements, density, vol% drainable liquids, and penetration resistance were measured. The percent drainable liquids were determined at 1 h, 2 h, 24 h, and 7 d in 250-mL graduated cylinders. Penetration resistance was measured at 24 h and 7 d using an Acme Penetrometer.

Results and Discussion

The results of the flow calculations prepared with supernate are listed in Table 18. Similar results for grouts produced with the composite waste are shown in Table 19. In all cases with the supernate grouts, the Reynolds number increased with the additional shear time, while in the composite grouts, the Reynolds number decreased. This effect is probably due to the thixotropic nature of the grouts produced with the supernate. Of these grouts, only the one made with a mix ratio of 8 lb/gal satisfied the turbulent flow requirement at the reference pumping conditions when measured at increasing shear rate. However, after 5 min of extended shearing, as would be encountered during transport in the pipeline, the grouts became thinner and all three had Reynolds numbers greater than the 2100 required for turbulent flow. The opposite effect was observed for the grouts produced with the composite waste, where increased

TABLE 18. Flow Calculations for Grouts Produced with Waste #766 Supernate. Dry solids consisted of 40 wt% cement, 48 wt% fly ash, and 12 wt% attapulgite.

	8 lb/gal		8.5 lb/gal		9 lb/gal	
	Up ^(a)	Down ^(b)	Up	Down	Up	Down
Grout density, lb/gal	13.0	13.0	13.1	13.1	13.23	13.23
Apparent viscosity, cP	36.7	31.6	48.3	30.2	58.2	36.5
Fluid consistency index, K'	0.0026	0.0011	0.0258	0.0022	0.0380	0.0019
Flow behavior index, n'	0.80	0.92	0.48	0.80	0.45	0.85
Reynolds number	2893	3662	1753	3543	1436	3065
Pressure loss, psi	4.3	4.2	6.1	8.5	7.5	4.4

(a) "Up" refers to the data collected while increasing the shear rate up to 1170/s.

(b) "Down" refers to the data collected while decreasing the shear rate from 1170/s after 5 min at the maximum shear.

TABLE 19. Flow Calculations for Grouts Produced with Waste #766 Composite. Dry solids consisted of 40 wt% cement, 48 wt% fly ash, and 12 wt% attapulgite.

	8 lb/gal		9 lb/gal	
	Up ^(a)	Down ^(b)	Up	Down
Grout density, lb/gal	13.22	13.22	13.69	13.69
Apparent viscosity, cP	37.7	66.6	63.1	229.7
Fluid consistency index, K'	0.0043	0.0532	0.0042	0.6521
Flow behavior index, n'	0.73	0.42	0.81	0.21
Reynolds number	2720	1224	1793	316
Pressure loss, psi	4.4	8.8	6.2	35.2

(a) "Up" refers to the data collected while increasing the shear rate up to 1170/s.

(b) "Down" refers to the data collected while decreasing the shear rate from 1170/s after 5 min at the maximum shear.

shear time resulted in a thickening of the grout and a dramatic decrease in the Reynolds number. Table 20 lists the percent drainable liquids and penetration resistances of the grouts. The main difference between the two types of grouts was the zero penetration resistance of the composite grouts. This same phenomenon was also observed in grouts prepared with cladding removal wastes (CRW), which contain substantial amounts of fluoride as a precipitate. Compressive strength measurements, conducted on three 2-in. cubes of grout produced with supernate at 9 lb/gal, indicated an average compressive strength of 617 psi, well above the 50 psi minimum. Strength tests were not conducted for any of the other grouts.

Conclusions

Based on the flow properties, the drainable liquids, and the penetration resistance, the only grout produced with the reference dry-solids blend that may satisfy the current process criteria is that made from the supernate at a mix ratio of 9 lb/gal. However, minor modifications to the dry-solids blend and better insight into the actual shear history of the process would certainly lead to grout formulations that meet all operational and performance criteria. In addition, the effects of blending this waste with other candidate TGF wastes on the grout properties must be determined to ensure reliable and safe operations.

TABLE 20. Percent Drainable Liquids and Penetration Resistance for Grouts Produced with Waste #766. Dry solids consisted of 40 wt% cement, 48 wt% fly ash, and 12 wt% attapulgite.

Mix ratio, lb/gal		<u>Supernate</u>		<u>Composite</u>	
		8.5	9	8	9
Phase separation, vol%	1 h	1.01	0.81	0.80	0
	2 h	1.81	0.81	1.20	0.04
	24 h	1.62	0	ND ^(a)	0.04
	7 d	ND	0	1.02	0
Penetration resistance, psi	24 h	160	172	0	0
	7 d	ND	2080	0	0

(a) ND = not determined.

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APPENDIX A

PRECIPITATION

APPENDIX A

PRECIPITATION

Additional information on Cu and Zr precipitation is included in this appendix.

FIGURE A.1. Precipitation of Cu from Tank 10 Using Oxalic Acid at $>30^\circ\text{C}$

TABLE A.1. Concentration of Zr and Na After Precipitation with NaF, NaOH, and NaNO₃

	<u>Al</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Na</u>	<u>Ni</u>	<u>Si</u>	<u>Zr</u>
Feed concentration, mg/L	300	75	110	222	748	36	9,815	37,100
	NaF at 95% Stoichiometry and 20°C							
Filtrate, mg/L	300	78	100	210	980	40	6,200	4,200
Percent reduction	0	0	9.1	5.4	-	0	36.8	88.7
	NaOH at 75% Stoichiometry and 20°C							
Filtrate, mg/L	131	81	107	242	1,354	38	4,707	2,240
Percent reduction	56.3	0	2.7	0	-	0	52.0	99.7
	NaOH at 75% Stoichiometry and 20°C - Repeat							
Filtrate, mg/L	367	82	112	226	3,600	41	2,044	33,000
Percent reduction								
	NaOH at 95% Stoichiometry and 20°C							
Filtrate, mg/L	174	74	107	211	2,680	41	2,425	13,300
Percent reduction								
	NaOH at 100% Stoichiometry and 20°C							
Filtrate, mg/L	157	67	101	201	3,254	29	2,109	11,900
Percent reduction								
	NaOH at 150% Stoichiometry and 20°C							
Filtrate, mg/L	166	70	103	205	8,083	32	654	11,800
Percent reduction								
	NaOH at 200% Stoichiometry and 20°C							
Filtrate, mg/L	253	72	105	203	21,705	36	287	33,500
Percent reduction								
	NaOH at 200% Stoichiometry and 20°C - Repeat							
Filtrate, mg/L	312	77	106	214	22,700	36	232	31,600
Percent reduction								
	NaNO ₃ at 75% Stoichiometry and 20°C							
Filtrate, mg/L	323	76	107	217	3,500	37	1,870	24,000
Percent reduction								
	NaNO ₃ at 100% Stoichiometry and 20°C							
Filtrate, mg/L	306	75	105	208	6,300	37	770	23,000
Percent reduction								
	NaNO ₃ at 100% Stoichiometry and 40°C							
Filtrate, mg/L	312	78	105	210	6,600	37	829	23,700
Percent reduction								
	NaNO ₃ at 200% Stoichiometry and 20°C							
Filtrate, mg/L	306	75	104	207	22,400	35	167	23,300
Percent reduction								

APPENDIX B

ELECTROWINNING

APPENDIX B

ELECTROWINNING

Laboratory data on addition of sulfamic acid and urea to HNO_3 electrolytes and on the relationship between air sparging rate and electrode spacing on voltage drop are included in this appendix. Additionally, an equipment list for a proposed pilot-scale electrowinning system is included.

Recycle of Cu Strip Solutions Using Cooled-Solution Electrowinning

A block diagram of the proposed continuous electrowinning system is shown in Figure B.1. A list of equipment and costs was prepared and is shown in Table B.2.

TABLE B.1. Urea (Ur) and Sulfamic Acid (SA) Required to Electrowin Solutions Containing 3.4 N to 3.9 N HNO₃ and 100 g/L Cu at 100 ASF

Temperature, °C	Weight Ratio, g SA/g Cu	Current Efficiency, %	Current Efficiency Error, %
40	0	0	0
"	0.1	64	10
"	0.2	100	14
"	0.2	100	10
"	0.3	84	10
"	0.4	66	9
"	0.5	74	10
"	1.0	81	10
New soln			
40	0.1	0	0
"	0.2	72	4
"	0.2	73	5
"	0.3	77	4
"	0.4	69	3
"	0.5	71	3
"	1.0	81	4
60	0.1	0	8
"	0.2	81	8
"	0.3	70	8
"	0.4	74	8
"	0.5	72	8
"	1.0	85	8
g Ur/g Cu			
40	0.3	0	0
"	0.4	0	0
"	0.6	63	9
"	0.8	63	9
"	1.0	67	7
60	0.3	0	0
"	0.4	0	0
"	0.6 (a)	0	0
"	0.7	53	9
"	0.8	40	8
"	1.0	50	9

(a) The rate of dissolution equaled the rate of deposition.

FIGURE B.1. Flowsheet for the Proposed Electrowinning Pilot Plant

TABLE B.2. Equipment and Costs for the Pilot Plant/Full-Scale System.
Includes both capital and expense items.

Description of Equipment	Justification	Estimated Cost, \$K
Rotary drum precoat filter - 0.3 m ²	Required to remove gel-like silicious material from process tank solutions before disposal or regeneration; could also be used to filter anolyte or to evaluate precipitation techniques	19
Cooling system Chiller - 1100 kcal refrigeration	Required to reduce the strip solution temperature in the refrigerated hold tank and to remove the heat generated in the electro-winning cell	15
Heat exchanger Panel coils	Required to remove the heat from the electro-winning cell	4
Refrigerated hold tank - air sparged	Required to reduce the solution temperature and to provide additional air sparging	5
Electrowinning cell Power supply 9600 A, 6 V	Required to supply the power to the electro-winning cell	18
Cell - 950 L air sparged	Required as an electrochemical reactor and an air sparging tank	6
Cell hardware - anodes/cathodes	Required to complete the electrowinning cell	10 (expense)
Hoist	Required to remove the electrodes from the cell	2 (expense)
Vent system	Required to remove NO _x from the refrigerated hold tank and from the electrowinning cell	5 (expense)
Hold tank - 1900 L	Required to hold tank 10 solution for use in the pilot plant	0.5 (expense)
Total equipment cost		84.5
Capital		67
Expense		17.5

FIGURE B.2. Potential Drop as a Function of Air Sparge Rate at Ambient Temperature with an Electrolyte Containing 3.6 N HNO_3 and 98 g/L Cu

(a)

(b)

FIGURE B.3. (a) Energy Consumption as a Function of Electrode Spacing Within a Cell Containing a Polypropylene Diaphragm and an Electrolyte Containing 3.8 N HNO_3 and 98 g/L Cu at Ambient Temperature; (b) Potential Drop as a Function of Electrode Spacing Under the Same Conditions

APPENDIX C

ANION EXCHANGE

APPENDIX C

ANION EXCHANGE

C. L. Matsuzaki

F. T. Hara

INTRODUCTION

UNC requested that PNL develop a method of disposal for 300 Area U-Cu-Tc bearing process waste. A method was developed to neutralize the waste with NH_4OH ; this precipitates the uranium and forms a liquid that has potential use as a fertilizer. Discovery of technetium in the neutralized waste as well as the presence of Cu and traces of U made it necessary to remove these elements before use.

SUMMARY

This report describes:

- Batch sorption studies using an anion resin in the NO_3^- form that gave Tc R_d values greater than 200 for a pH range from 7 to 10.
- Batch sorption studies using cation resins that gave excellent R_d values for Cu and U.
- An ion-exchange column experiment that showed a 50% breakthrough for Tc at 90 column volumes.

FEED SOLUTION PREPARATION

Feed solution for ion-exchange column studies was prepared. Tank 32 (71 L) containing U, H_2SO_4 , and HNO_3 plus tank 16 (7 L) containing $\text{Al}(\text{NO}_3)_3$ and HNO_3 were mixed and slowly neutralized with 98 L of NH_4OH to precipitate the U (present at ~ 70 g/L). After the U sludge was removed by settling, approximately 130 L of feed solution was decanted off. Analysis of the pH 9.6 solution showed the following:

<u>Element</u>	<u>Concentration, $\mu\text{g/mL}$</u>
U	0.64
Tc	0.354
Al	12
Cu	21

BATCH SORPTION

Technetium in solution is present as the pertechnetate ion, TcO_4^- . Prior work at the Hanford PUREX plant has indicated that an anion resin such as Dowex 1-X8 should be an efficient resin. In order to ensure this, batch sorptions with Dowex 1-X8 were performed.

Batch sorption involves contacting a weighed portion of resin with a known volume of solution. Five solutions of pH values 7.3, 8.3, 9.0, 9.5, and 10.0 were prepared by NH_4OH neutralization of tank 32 solution to determine R_d as a function of pH. Approximately 0.1 g (wet weight) of resin was placed in a plastic bottle, to which 10.0 mL of solution was added. Samples were placed on a shaker for ~16 h sorption. The solution was filtered, neutralized with 8 M HNO_3 , mixed with PCS,[®] and placed into a liquid scintillation counter for analysis.

Table C.1 indicates the method used to calculate the R_d values for the resins, as given in Table C.2. R_d values of 186 to 280 were found for the pH range 7 to 10, with slightly better results for the 50 to 100 mesh resin.

Additional batch sorptions were determined for Cu and U using a variety of cation and anion resins. The most efficient resins are presented in Table C.3. In general, better results are obtained for cation removal at a lower pH. Aluminum is also removed by the resins; two phenolic resins gave Al R_d values greater than 200.

[®] PCS: a proprietary reagent of Amersham Corporation, Arlington, Illinois.

TABLE C.1. R_d Calculation

$$R_d, \text{ mL/g} = \frac{\text{standard-sample}}{\text{sample}} \times \frac{\text{contact volume}}{\text{resin weight} \times F}$$

given in scintillation counts or $\mu\text{g/mL}$

$$\text{where } F = \frac{\text{resin weight after drying}}{\text{resin weight before drying}}$$

$\frac{R_d}{\text{mL/g of resin}} \approx \frac{\text{column volume to 50\% breakthrough}}{\text{which is total column capacity.}}$

TABLE C.2. Dowex 1-X8 Batch Sorption

pH	R_d Values for Tc	
	20-50 Mesh	50-100 mesh
7.3	192	220
8.3	192	280
9.0	186	211
9.5	211	229
10.0	200	234

TABLE C.3. Other Resin Batch Sorptions

Resin	U R_d Values		Cu R_d Values		Tc R_d Values	
	pH 7.3	pH 10.0	pH 7.3	pH 10.0	pH 7.3	pH 10.0
Cs-346 (cation)	1.6×10^6	253	3983	8	18	17
Dowex 1 (anion)	54	0	0	0	221	240

ION-EXCHANGE COLUMN STUDY

An ion-exchange column with a 200 mL capacity was set up with a 15 L feed solution tank and a sample fraction collector. The parameters for the study are given in Table C.4. The system ran continuously for over 2 1/2 days with 1200 samples collected (one approximately every 30 minutes).

Samples for scintillation counting were prepared by neutralizing 1 mL with 2 mL 8 M HNO_3 before the addition of 15 mL PSC® scintillation cocktail. Without the addition of HNO_3 , the basic sample did not form a homogeneous solution with the PCS; HNO_3 blank samples indicated no acid interference during scintillation counting.

Figure 1 shows the Tc breakthrough as a function of column volumes loaded. C/C_0 is the ratio of the "activity" of the sample counted to the "activity" of the feed solution. The 50% C/C_0 value can be used to determine the total capacity of the resin bed:

$$90 \text{ col vol} \times 0.354 \text{ ml/L Tc} = 31.9 \text{ mg/L of resin}$$

C/C_0 values in Figure C.1 for 10 to 20 column volumes were less than background. This experiment demonstrated that Tc can be effectively removed from the neutralized process waste stream.

SUGGESTED FUTURE STUDIES

Several more ion-exchange runs should be completed to obtain engineering scale-up data; one parameter that should be changed is the feed solution flow rate. Also, the feed solution should be adjusted to a lower pH to measure its effect on loading; although batch sorption studies indicated little effect of pH, a different behavior may be seen for an ion-exchange column study. Lowering the pH would mean that the Tc, as well as U and Cu, could be removed simultaneously with anion and cation resin columns in series.

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FIGURE C.1. Technetium Breakthrough on Dowex 1-X8

APPENDIX D

ACID PURIFICATION UNIT

APPENDIX D

ACID PURIFICATION UNIT

APU CYCLE

One APU cycle consists of the following six steps:

Step 1

The first step is water displacement. Air pressure forces the acid level in the acid reservoir down from the first electrode to the second electrode; see Figure D.1. This pushes the water in the resin chamber into the water reservoir. The water level in the water reservoir will consequently rise from the third electrode to the vicinity of the second.

Steps 2 and 3

The by-product and the water makeup occur next. Air pressure continues to force the acid feed down past the second electrode to the third electrode. The feed solution is forced through the resin and into the by-product line. The copper by-product is collected in a carboy. Simultaneously, water is added to the water reservoir. The level is raised up automatically to the #1 electrode.

Step 4

The fourth step, acid displacement, is similar to the water displacement in Step 1. Now, air pressure pushes the water level in the water reservoir from the first electrode to the second electrode. The water goes through the resin and pushes the feed solution in the resin chamber back into the acid reservoir. Because of lesser affinity of the copper to the resin than the acid, the metal compounds are displaced from the bed, leaving the acid to be washed out as product.

FIGURE D.1. Fluid Levels in the APU Cycle Steps

Steps 5 and 6

The final steps are the product and acid makeup. The water continues part the second electrode to backwash the resin. The purified acid is collected and the water level falls to the third electrode. At the same time, the pump is turned on automatically and the acid reservoir is filled to begin the cycle again.

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