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WASTE ACID DETOXIFICATION AND RECLAMATION

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ABSTRACT

A prototype Waste Acid Detoxification and Recovery System (WADRTM), originally developed by the Pacific Northwest National Laboratory (PNNL) for Tinker Air Force Base, was tested at the Watervliet Arsenal in Watervliet, New York. The unit demonstrated the ability to concentrate waste acids produced by plating operations at the Arsenal so that they may be recycled. Currently, waste acids at the Arsenal are not concentrated enough to be recycled and must be disposed of. The WADRTM unit typically produced recycled acids at a concentration 8% higher than the incoming waste acid allowing the acid to be recycled back to process. Economic analysis on the installation of the WADRTM system at the Arsenal indicates that over \$100,000 per year may be saved over the current method of waste acid handling.

INTRODUCTION

Large quantities of metal-bearing spent acids are produced by electroplating, surface finishing, and chemical milling/dissolution operations common to the Department of Energy (DOE) and the Department of Defense (DOD). The intent of this study was to provide initial data to prove the efficacy of using a prototype system developed by the Pacific Northwest National Laboratory (PNNL) to recover and recycle such spent acids. The system tested is termed the Waste Acid Detoxification and Recovery System (WADRTM).

The Watervliet Arsenal, located in Watervliet, New York, has a waste stream of concentrated acids that is generated by the chrome plating line. The Arsenal has been asked by regulators to address this highly reactive and low pH waste. The WADRTM system was uniquely suited to handle this waste, using a combination of proven methods with advanced materials.

The prototype WADR™ system was originally developed and tested for Tinker Air Force Base, but refurbishments in the plating shop at Tinker AFB prevented the system from being installed. The system was subsequently transferred to the Watervliet Arsenal for initial testing at the chrome plating line and permanent installation at the vessel plating line. This report describes the tests conducted, the operability of the system and its effectiveness.

PROCESS DESCRIPTION

The WADR™ unit, as manufactured by Pacific Northwest National Laboratories (PNNL), is essentially a batch vacuum distillation unit. Major components of the system include a reboiler tank, steam heated reboiler, vacuum column, water-cooled condenser, condensate tank, and other support equipment. The unit also came equipped with a crystallizer for removing accumulated heavy metal salts, but this was not used during the demonstration. The use of flouropolymer liners reinforced with thermosetting plastic makes the WADR™ system capable of handling the most highly reactive solutions. A block-flow diagram is shown in Figure 1 (all components are not shown).

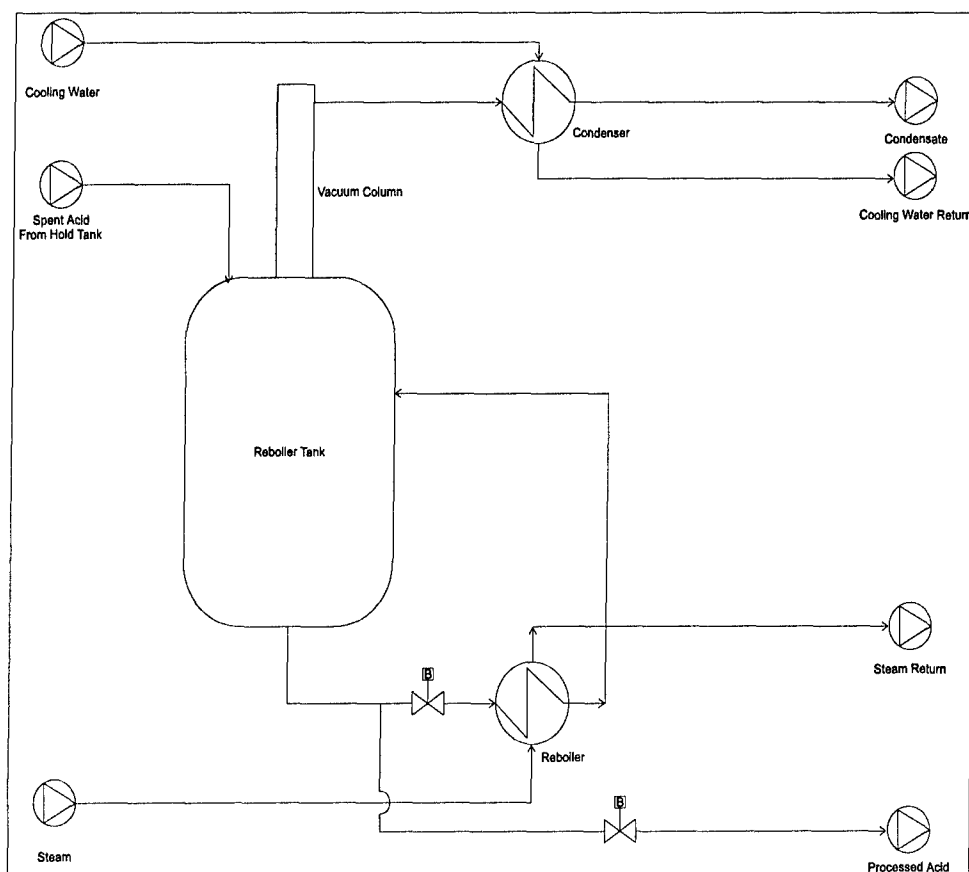


Figure 1: Block-flow Diagram of WADR™ System - Batch Distillation

Spent acid, diluted during manufacturing and containing iron contaminants, enters the system from a 3400 gallon holding tank in 200 gallon batches. The acid is concentrated until the boiling point temperature reaches a temperature consistent with an adequately dewatered acid solution. At that point the batch is removed from the reboiler tank and returned to the holding tank used in manufacturing. The system is placed under vacuum to lower the boiling point of waste acid to be recycled. Lower boiling points achieved through placing the system under a vacuum, allow for longer equipment life and lower energy costs.

EXPERIMENTAL

The WADR™ system was operated on six separate occasions to recycle manufacturing acids. The mode of operation in each case was the following:

- 1) A sample from a 3400 gallon holding tank was taken and assayed for Fe, acid A, and acid B. These concentrations were used as "initial" values.
- 2) The WADR™ system was charged with 200 gallons of metal-bearing, dilute acid solution from the holding tank.
- 3) The WADR™ system was operated until the boiling point of the charge had reached a temperature consistent with recycled acid.
- 4) Upon achieving an adequate boiling point, WADR™ operation was halted and a sample was taken from the batch tank. This sample was assayed for Fe, acid A, and acid B. These concentrations were used as "final" values.
- 5) The concentrated charge was returned to the 3400 gallon holding tank.
- 6) A sample was taken from the holding tank after the addition of the distilled charge and assayed for Fe, acid A, and acid B.

Samples were collected in HDPE containers and analyzed within 7 days. Acid samples were analyzed via titration and Fe concentrations were analyzed by Inductively Coupled Plasma (ICP). Steam consumption was determined by valving and pipe sizes. Cooling water consumption was determined by valving and pipe sizes. Electrical demand on the system was determined by calculation based on loadings marked on supporting equipment.

RESULTS

The results obtained during the demonstration are shown in Table 1. Acid content in the processed 200 gallon batches was raised 8% for acid A and 8% for acid B. Iron contents were also raised, on average, from 2.8 to 3.4 ppm. Processing times for 200 gallon batches averaged 12 hours. During this time, 220 lbs of steam were used, 1320 gallons of cooling water, and 30 kW-Hr of electricity were used. Data from Table 1 was used to calculate concentration factors. The data obtained on December 7th was not used in calculations, because this represents a 1 hour processing time that proved to be insignificant. Figures 1 and 2 express the results graphically.

Table 1: Results Expressed as a Percentage of Specification

Date	Gallons Processed	Initial Acid A	Initial Acid B	Initial Fe	Conc. Factor	Max Outlet Temp	Final Acid A	Final Acid B	Final Fe
16-Sep	200	94.01%	92.78%	-	7%	250	100.59%	99.27%	-
3-Oct	200	95.00%	98.27%	-	8%	250	102.60%	106.13%	-
18-Oct	200	95.03%	98.54%	2.60	10%	260	104.62%	108.91%	4.00
16-Nov	200	94.56%	98.98%	2.90	8%	257	102.49%	105.69%	3.10
17-Nov	200	95.62%	99.27%	2.90	8%	-	104.14%	107.30%	3.00
7-Dec	200	96.80%	103.80%	0.50	0%	275	96.80%	103.65%	0.60

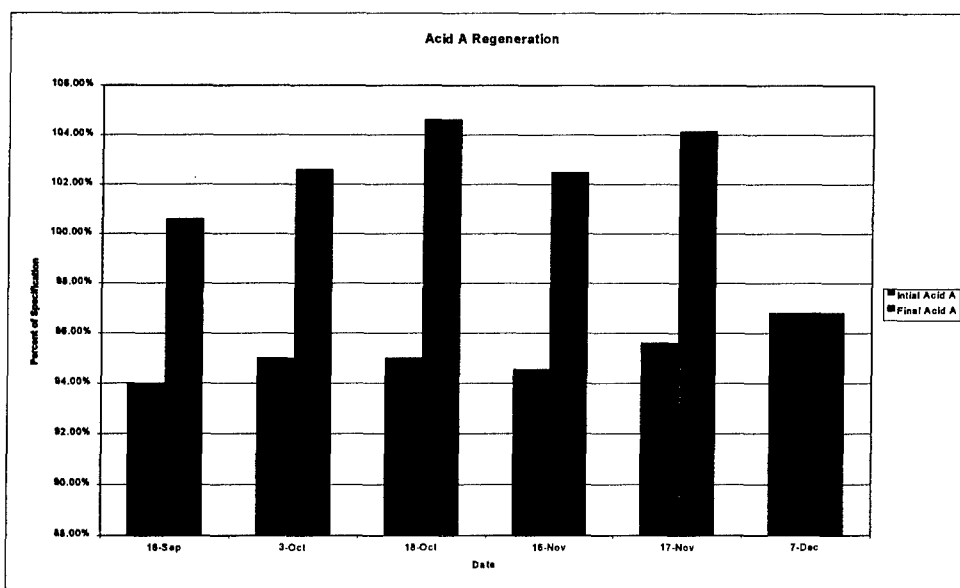


Figure 2: Acid A Concentration

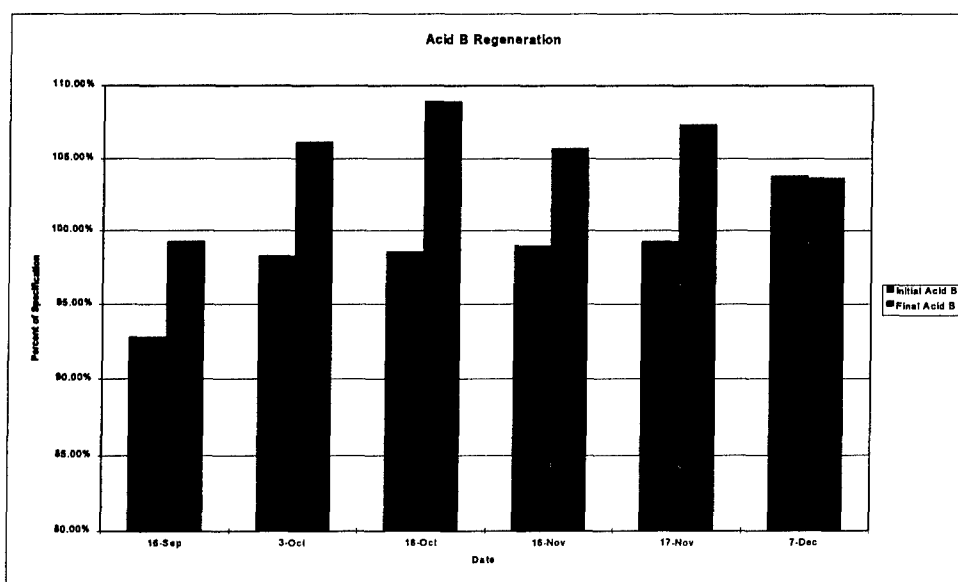


Figure 3: Acid B Concentration

DISCUSSION

A rough economical analysis can be performed on the system as tested. Typically during periods of high output, the 3400 gallon acid holding tank would have to be emptied and recharged with fresh solution. Normal levels of production activity dictate that this recharging operation be carried out 4 times a year on two 3400 gallon tanks. The cost of this operation amounts to \$193,528 per year which includes material as well as disposal costs. By using the WADR™ unit the acid can be recycled. Using the average concentration factor found during testing (8%), acid additions can be limited to \$15,958 per year and disposal costs to \$9,828 per year. Adding in the cost of utilities to operate the WADR™ unit this figure becomes a total cost of \$27,576 per year. This represents a savings to the arsenal of over \$165,000 per year. When this savings

is discounted to net present value terms using a rate of 4.8% with the initial cost of the WADR™ unit set at \$200,000 and an expected machine life of ten years, annualized savings amount to \$109,000 over the present operation.

Using the same economic model it can be seen that the total net savings realized by the installation and operation of a WADR™ unit at the Watervliet Arsenal is heavily effected by the concentration factor achieved during processing. Figure 4 shows the relationship between the concentration factor and net present value savings over a ten year life span. It can be seen that the savings realized by utilizing a WADR™ system levels off at a concentration factor around 8%.

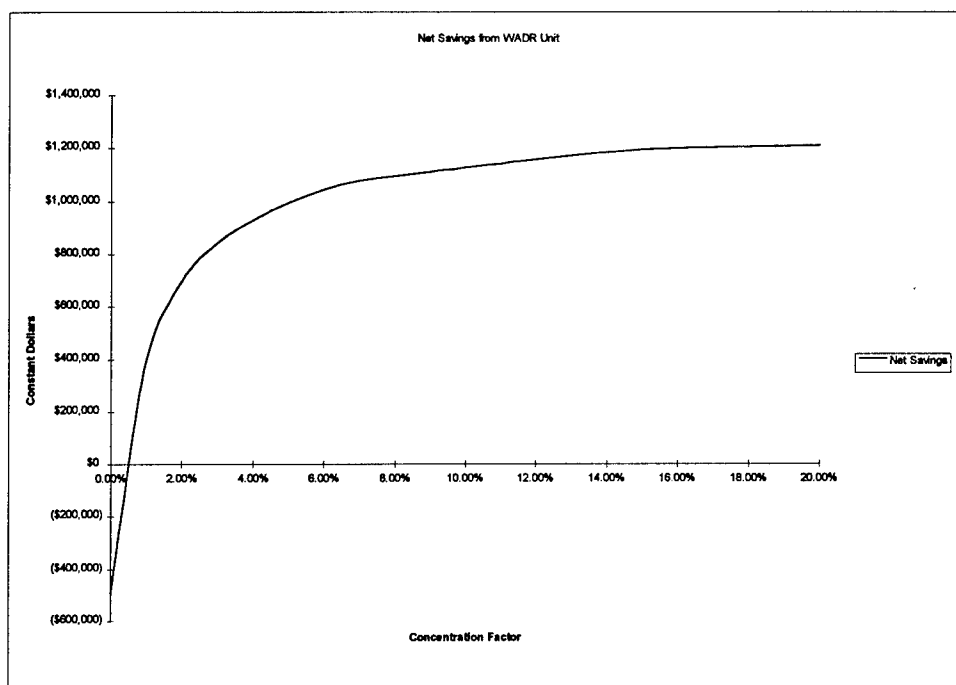


Figure 4: Savings as Related to Concentration Factor

In addition to the importance of the concentration factor in determining the economic viability of the WADR™ system, waste throughput is also a concern. Figure 5 shows the effect that waste throughput has on the economic viability of the system. Each change-out represents one 3400 gallon acid tank. During time of normal manufacturing activity the Arsenal will require 8 change-outs to maintain the acid tanks within concentration specification, resulting in an annual savings of around \$100,000. At lower manufacturing levels, annual savings drop off in a linear fashion. With just four change-outs per year a savings of only \$40,000 will be realized over a 10 year equipment life.

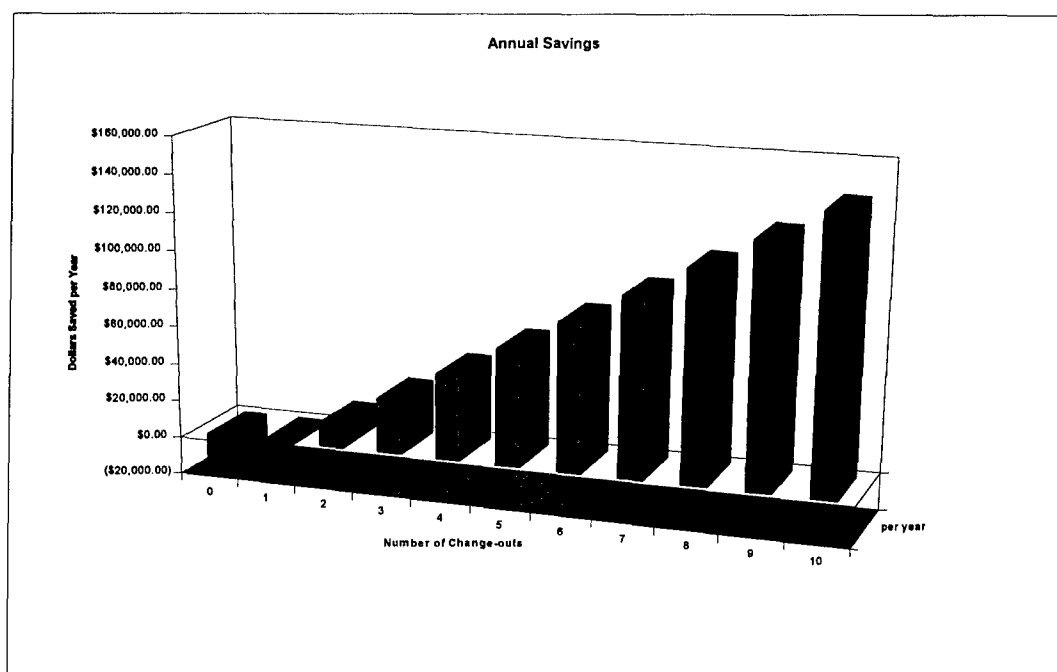


Figure 5: Annualized Cost Savings Based on WADR™ Usage

CONCLUSIONS

The WADR™ system as tested at the Watervliet Arsenal performed as expected. Acid concentrations were raised an average of 8% across the unit enabling the Arsenal to save over \$100,000 per year in reduced acid and waste costs. Economic analysis reveals that savings produced by the WADR™ system are tied proportionally with its use over a 10 year life span. In addition to the economic savings that can be realized, improved process control will also result. The current system of operation produces large swings in acid concentration. By utilizing the WADR™ system, acid concentrations can be maintained at near constant levels resulting in a well defined process that produces a more constant quality product. Another area of importance that is difficult to measure in dollar terms is the importance of reduced reagent and waste disposal in today's manufacturing arena. Permanent installation of the WADR™ system will enable the Watervliet Arsenal to operate a "green" process with respect to its acid disposal issues.