Rejuvenation and Recovery of Electroplating Acids Using the WADR Technology

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ABSTRACT

Acid baths at the U.S. Air Force/Oklahoma City Air Logistic Center (OC-ALC) will be rejuvenated by the use of a new technology—Waste Acid Detoxification and Reclamation (WADR), a distillation process that concentrates the metals and creates a clean reuseable acid. The concentrated metals are recovered for disposal or recycling. A 200-gallon batch prototype system will be installed and demonstrated on HCI, HNO_3 and H_2SO_4 baths at OC-ALC's electroplating shop in late 1994. The system was tested in the summer of 1994 with typical industrial spent acids. The design and early demonstration testing is supported by the joint U.S. Department of Energy/USAF Memorandum of Understanding (MOU) program. The WADR system is expected to reduce waste from the OC-ALC acid baths by 80% to 90% as compared with current treatment operations. Laboratory test results and the prototype system design are presented here. The technology is expected to meet the needs of various industries generating spent acids with increasing disposal costs.

INTRODUCTION AND TECHNICAL DISCUSSION

Electroplating shops generate significant volumes of spent/waste acids, as do many other, process industries. The volume, concentration and contaminants in the waste acids vary widely, but all represent an increasingly difficult and expensive waste disposal problem. The electroplating shop at the U.S. Air Force/Oklahoma City Air Logistics Center (OC-ALC) has several acid baths that are dumped after metal contaminant concentrations interfere With continued use, which not only slows operations but creates a waste stream that must be treated prior to disposal. A pollution prevention and waste reduction program, conducted by Battelle, identified and evaluated potential solutions to this problem.

The technology being demonstrated here for treating spent electroplating acids is the Waste Acid Detoxification and Reclamation (WADR) process[1] developed at Pacific Northwest Laboratory through the U.S. Department of Energy (DOE). With this process, acids can be rejuvenated and recovered for reuse and metal by product reclaimed from various spent/waste acid streams. Acid recoveries and waste reductions vary with the spent acid composition and client requirements. The combination of simple and proven distillation technology and advanced corrosion-resistant materials results in a system that reduces raw material and waste disposal costs while providing a clean process acid for improved process quality.

For this program the WADR system was tested with various acid samples representative of OC-ALC acid baths. A prototype batch system was designed for demonstration at OC-ALC's electroplating shop in late 1994.

Sample Testing

The OC-ALC acid .baths that will be treated with the prototype WADR process include 14% HCI, 10% HNO_3, 12% H_2SO_4, and 40% H_2SO_4/l% HF. Samples of these acids were used for laboratory distillation testing to determine the initial acid and contaminant concentrations and the net recoveries and purities of the products. Table 1 gives the results of these tests.

As shown by the table, vacuum distillation of the HCI and HNO_3 solutions at 100°C and 85°C, respectively, produces a clean overhead condensate product. The metal

contaminants are concentrated in the still bottoms. Once concentrated, the metals can be recovered or disposed of in much smaller quantities (80% to 90% volume reduction) the original acid waste stream.

The sulfuric acid is concentrated in the still as water evaporates (from 65°C to 130°C) and is condensed as a relatively clean stream to be used as process makeup water or discharged. Crystallized metal salts are separated from the concentrated bottoms after cooling and filtration. Again, the metal contaminants are available for recovery or disposal.

Prototype Equipment and Design

The prototype system was designed and built by Viatec Recovery Systems, who is licensed to market and manufacture the WADR process commercially. A process flow schematic for the WADR prototype system is shown in Figure 1. A 200-gallon batch system was selected for OC-ALC to process the smallest acid bath in a single batch while larger volumes could be processed as multiple batches. The system is skid mounted with overall dimensions of 7 ft 6 in. wide x 12 ft long x 10 ft high.

The equipment is constructed of dual-laminate thermoplastic materials combining the corrosion resistance of fluoropolymer liners with the strength and economy of reinforced thermosetting plastic shells. This combination is capable of processing nearly any type of mineral acid.

The system operates under a vacuum to reduce distillation temperatures and side reactions, The low operating temperatures allow low-pressure steam to be used as the heat source in the reboiler. A significant volume reduction of waste (~80% to 90%) is achieved as the acid is recovered. For HCI and HNO_3, the overhead distillate product is clean and reusable representing 80% to 85% of the initial batch volume. The still bottoms with concentrated metal contaminants are cooled and disposed of as waste. Metal recovery is possible but is not currently planned at OC-ALC.

Performance Testing and Demonstration

The prototype system will be installed at OC-ALC during October 1994 and will be demonstrated and tested following system shakedown and operator training. Joint efforts among DOE, PNL and OC-ALC include a brief shakedown test at an industrial site prior to installation at OC-ALC. Both tests will demonstrate operating performance and waste reduction of the system.

Economic Benefit

Electroplating shops have historically dumped acid baths when contamination interferes with product quality. The contaminants frequently include toxic metals, such as cadmium, chromium or nickel, requiring that the waste be disposed/treated as hazardous waste at a significant cost. The WADR can specificantly reduce the disposal costs providing a payback period of less than 2 years. Table 2 summarizes the economic benefits for the OC-ALC application. Site specific costs may vary for waste disposal, metal recovery, low pressure steam, and labor. The benefit of reducing waste, and the associated costs, we expected to justify investing in a reliable, easy to operate recovery system.

CONCLUSIONS

The WADR system reduces costs for disposal of spent/waste acid baths while providing a clean acid for reuse. A waste reduction, and concurrent acid recovery, of 80% to 90% is possible. Because the metals can be recovered, the system helps alleviate environmental liability.

The demonstration of the prototype system at OC-ALC will validate the operating performance and process economics. Savings in makeup chemical costs are projected to result in approximately a 1-year payback for the WADR distillation system.

ACKNOWLEDGMENTS

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REFERENCE

1. Jones, E.O. and Kensington, K.L., 1993, "Spent Acid Recovery Using the WADR Process System," American Chemical Society, Division of Environmental Chemistry, August 1993, BN-SA-379GA Chicago, Illinois.

TABLE 1. LABORATORY TESTING RESULTS

Initial Composition	Distillate Composition	Bottom Composition	Distillate Recov. wt%	Initial Temp. °C	Final Temp. °C
11.5 wt% H_2SO_4 1000 ppm Fe 80 ppm Ni	Water with < 50 ppm SO_4	51 wt% H_2SO_4	77	55	80
39.0 wt% H_2SO_4 0.9 wt% HF 965 ppm Fe 925 ppm Ni	Water with 1.6 wt% HF	84 wt% H_2SO_4	52	65	158
9.8 wt% HNO_3 400 ppm Fe 31,700 ppm Ni	*8.2 wt% HNO_3 with < 1 ppm metals	17 wt% HNO_3	82	61	83
13.6 wt% HCl 1000 ppm Fe 45 ppm Ni	*9.7 wt% HCl with < 1 ppm metals	20 wt% HCl	87	57	99

- The HNO_3 and HCl can be easily recovered as concentrated acids by initially evaporating clean water, followed by recovery of the concentrated acid.

Note: All experiments were performed under a vacuum of 125 torr.

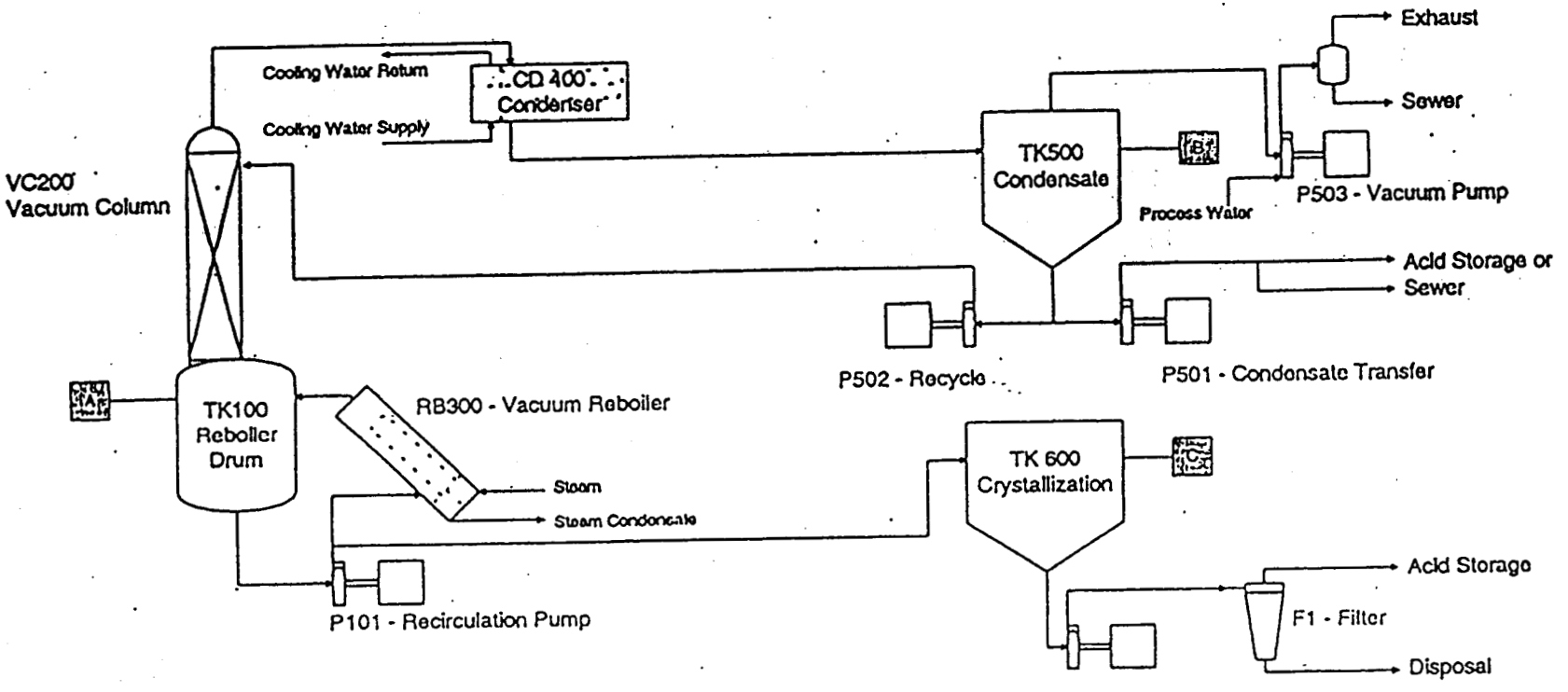

FIGURE 1. WASTE ACID DETOXIFICATION AND RECLAMATION (WADR)
PROCESS FLOW DIAGRAM DOE/USAF INTEGRATED PROGRAM

TABLE 2. OVERALL SAVINGS OF WASTE GENERATION

Description	Annual Quantity[1] gal/yr	Savings[2] $/gal	Total Savings
H_2SO_4	750	15.50	11,600
H_2SO_4/HF	3400	19.20	65,300
HNO_3	2300	11.40	26,200
HCl	3550	12.50	44,400
Total 10,000 gal			$147,500

1) The quantity (gal/yr) is based on the total bath volumes and assumes a dump every 24 months. There are a total of 25 separate baths for a total bath volume of 20,000 gal distributed as shown in the table.

2) The savings in $/gal is based on the estimated cost of waste disposal ($2/lb) versus the WADR operating cost, e.g., for H_2SO_4 it would be ($3645-$573)/200 gal = $1550 gal.