THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

Concurrent Technologies Corporation

ETV VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**ELECTRODIALYSIS**		
APPLICATION:	**CHROMIC ACID ANODIZE BATH MAINTENANCE**		
TECHNOLOGY NAME:	**RETEC^{Ò} Model SCP-6 Separated Cell Purification System**		
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The United States Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved, cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations, stakeholder groups consisting of buyers, vendor organizations, and states, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The ETV P2 Metal Finishing Technologies (ETV-MF) Program, one of 12 technology focus areas under the ETV Program, is operated by Concurrent Technologies Corporation, in cooperation with EPA's National Risk Management Research Laboratory. The ETV-MF Program has evaluated the performance of an electrodialysis technology for the purification of chromic acid anodize bath solution. This verification statement provides a summary of the test results for the USFilter RETEC® Model SCP-6 Separated Cell Purification System.

VERIFICATION TEST DESCRIPTION

The USFilter RETEC® Model SCP-6 (RETEC® unit) was tested, under actual production conditions, on a chromic acid anodize bath solution, at DV Industries, Inc. (DVI) in Lynwood, California. Chromic acid anodizing is performed on various aluminum parts in one of two independent parts processing tanks: a 27-foot or a 62-foot tank. The verification test evaluated the ability of the RETEC® unit to purify the chromic acid anodize bath solution of process contaminants in the 27-foot chromic anodizing tank.

Testing was conducted during two distinct 5-week test periods (Baseline and Operational Modes):

- During the first test period (Baseline Mode), the RETEC® unit was turned off, and the chromic acid anodizing bath was monitored to determine the buildup rate of process contaminants. Aluminum parts were anodized at typical processing rates for DVI.
- During the second test period (Operational Mode), the RETEC® unit was turned on, and the chromic acid anodizing bath was monitored to determine the rate of process contaminant removal. Again, aluminum parts were anodized at typical processing rates for DVI.

Historical operating and maintenance labor requirements, chemical usage, and waste generation data were collected to perform the cost analysis.

TECHNOLOGY DESCRIPTION

The RETEC® Model SCP-6 Separated Cell Purification System purifies and reconditions spent chromic acid anodizing solution by circulating it through a specialized electrochemical cell. Anodizing solution is recirculated between the anolyte section of the RETEC® cell and the anodizing process tank. During this process, trivalent chromium in the anodizing solution is oxidized to hexavalent chromium, and metal cations are transported to the catholyte solution through a porous, polymeric membrane separating the anolyte and catholyte compartments of the cell. The treated process solution is then returned to the anodizing bath. The metal contaminants removed from the process solution are kept in solution in the catholyte side of the cell until the solution becomes saturated with contaminants. At DVI, the RETEC® saturated catholyte waste (100 gallons) is disposed of about four times a year.

VERIFICATION OF PERFORMANCE

In the Baseline Mode, six weekly grab samples were collected over a five-week period from the anodizing tank and analyzed to determine the buildup rate of process contaminants. In addition, weekly grab samples from the rinse tanks upstream and downstream of the anodizing tank were collected and analyzed for mass balance purposes related to the anodizing tank. Rinse tank analyses showed dragout to be insignificant.

In the Operational Mode, five weekly grab samples were collected over a six-week period from the anolyte and catholyte sections of the RETEC® unit. All samples were analyzed for process contaminants in order to perform a mass balance and determine the removal efficiencies of process contaminants from the anodized bath solution.

Eleven weeks after the RETEC® unit was turned on (16 weeks after test started), samples were again collected from the RETEC® unit. These samples are designated as "1Q" in **Table i**, and represent the chemical characteristics of the anolyte and catholyte at the end of the first quarter of the catholyte operating cycle, 11 weeks after the RETEC® system was turned on.

Average analytical results for key parameters are shown in **Table i.** Hexavalent chromium is the primary active ion in the chromic anodizing process. Trivalent chromium is the natural occurring reduced state of hexavalent chromium. The reduction from hexavalent chromium to trivalent chromium occurs in the anodizing bath over a period of time, and can be accelerated by temperature and pH changes, and chemical and electrochemical reactions. Aluminum and magnesium are the primary anodizing bath contaminants. A small amount of aluminum (0.39 g/L) is required for the aluminum anodizing process to occur. After six weeks of RETEC®

operation, the purified chromic acid anodized solution maintained a relatively steady chemical and contaminant composition similar to the anodizing solution at the time of RETEC® start-up. The buildup of process contaminants in the anodizing solution was slowed, while the contaminant level in the catholyte increased dramatically, showing a contamination transfer across the polymeric membrane.

Sampling Week	Hexavalent Chromium (by titration) g/L Anolyte / Catholyte	Trivalent Chromium (by titration) g/L Anolyte / Catholyte	Total Chromium (by ICP-AES) g/L Anolyte / Catholyte	Total Aluminum (by ICP-AES) g/L Anolyte / Catholyte	Total Magnesium (by ICP-AES) g/L Anolyte / Catholyte
0 - Baseline	48.0/NA	<1.1/NA	49.0/NA	3.6/NA	0.27/NA
1 - Baseline	48.0/NA	<1.1/NA	46.0/NA	3.7/NA	0.31/NA
2 - Baseline	48.1/NA	<1.1/NA	42.0/NA	3.8/NA	0.25/NA
3 - Baseline	47.5/NA	<1.1/NA	43.0/NA	4.0/NA	0.26/NA
4 - Baseline	50.5/NA	<1.1/NA	50.0/NA	4.5/NA	0.32/NA
5 - Baseline	51.5/20.6	<1.1/<1.1	46.0/18.0	4.5/0.1	0.32/0.09
6 - Operational	52.6/21.3	<1.1/<1.1	44.0/20.0	4.1/2.0	0.29/0.12
7 - Operational	52.9/22.5	<1.1/<1.1	44.0/21.0	4.1/3.2	0.22/0.15
8 - Operational	53.5/36.1	<1.1/<1.1	48.0/34.0	4.6/3.8	0.24/0.20
9 - Operational	53.8/41.5	<1.1/1.7	46.0/42.0	4.4/5.4	0.21/0.25
10 - Operational	Thanksgiving holiday – no samples collected this week				
11 - Operational	52.7/51.6	<1.1/<1.1	50.0/48.0	4.9/6.4	0.24/0.28
16 - 1Q	NA	NA	52.5/50.5	5.4/7.5	0.26/0.31

Titration = Standard sodium thiosulfate titration, 1999 Metal Finishing Guidebook, Vol. 97, No. 1, Control, Analysis, and Testing Section – Chemical Analysis of Plating Solutions, Charles Rosenstein and Stanley Hirsch, Table VIII – Test Methods for Electroplating Solutions, page 538.
ICP-AES = Inductively Coupled Plasma-Atomic Emission Spectrometry (EPA SW-846 Method 6010B)
NA = Not Applicable

Table i. Summary of Key Analytical Data

Oxidation of Trivalent Chromium to Hexavalent Chromium. The oxidation of trivalent chromium to hexavalent chromium in the anolyte and the transfer of hexavalent chromium across the polymeric membrane from the catholyte to the anolyte by the RETEC® unit is marketed as one of the beneficial conversions performed by the electrochemical process. However, as can be seen in **Table i**, trivalent chromium levels were never above background levels in the anolyte; therefore, there was no quantifiable oxidation to hexavalent chromium. A slight increase in hexavalent chromium levels in the anolyte was observed, but since DVI adds chromic acid to the anodizing bath on a regular basis, this increase in hexavalent chromium concentration can not be definitively attributed to the RETEC® electrolytic reaction. Hexavalent chromium levels measured by titration that are higher than total chromium levels measured by ICP-AES are due to uncertainties inherent in the precision of these two different analytical methods.

Contaminant Removal. Removal of the primary contaminants of the chromic acid anodize bath solution, aluminum and magnesium, are shown in **Table ii**. For the Baseline Mode, the average aluminum increase in the anolyte was 0.180 g/L per week. The average magnesium increase in the anolyte was 0.010 g/L per week. During the Operational Mode, aluminum and magnesium levels in the anolyte remained relatively stable, while the catholyte showed an overall increase of 6.32 g/l of aluminum. The total volume of catholyte solution at the end of the verification test was 392 gallons (150 gallons in the clarifier + 30 gallons in the RETEC® cell and piping + 212 total gallons of catholyte overflow collected during the test). Multiplying the aluminum contamination increase in the catholyte by the total catholyte volume gives an overall removal of 9,378 grams of aluminum from the anolyte solution over the six week test period (6.32 g/l x 392 gallons x 3.7854 liters/gallon =

9,378 grams). The increase in magnesium contamination of the catholyte was less pronounced, showing an overall increase of 0.19 g/l. Multiplying the magnesium contamination increase in the catholyte by the total catholyte volume gives an overall removal of 282 grams of magnesium from the anolyte solution over the six week test period (0.19 g/l x 392 gallons x 3.7854 liters/gallon = 282 grams). The RETEC® unit proved to be an adequate technology for removing aluminum contamination from the chromic acid anodize solution at DVI; however, the unit was not able to completely arrest the contamination rise in the anodizing bath. Since the six-cell model installed at DVI is the smallest RETEC® unit made by USFilter, it is possible that a larger unit may solve this problem. However, since the RETEC® unit was turned on when the anodizing bath was within 1.6 g/L of its upper limit for aluminum, the purification system was unable to prevent the anodizing bath from reaching the upper contamination limit triggering disposal of the anodizing bath. It can be concluded that the RETEC® system extended the anodizing bath life by slowing the contamination build-up rate, but due to the relatively short verification test period, the length of this extension could not be determined.

Anolyte		**Start (g/L)**	**End (g/L)**	**Change (g/L)**	**Average Weekly Increase (g/L)**
Aluminum	Baseline Mode	3.6	4.5	+0.9	+0.180
	Operational Mode	4.5	4.9	+0.4	+0.067
Magnesium	Baseline Mode	0.27	0.32	+0.05	+0.010
	Operational Mode	0.32	0.24	-0.08	-0.0133
Catholyte					
Aluminum	Operational Mode	0.085	6.40	+6.32	+1.053
Magnesium	Operational Mode	0.087	0.28	+0.19	+0.0317

Table ii. Contaminant Removal

Energy Use. Energy requirements for operating the RETEC® unit at DVI include electricity for the anolyte and catholyte pumps and the system rectifier. Electricity use was determined to be 6,366 kWh/day, based on continuous operation of the system.

Waste Generation. A waste generation analysis was performed using operational data collected during the verification test period, and historical records from DVI. Waste generation data normalized to the amount of work processed over the verification test period showed an anodizing bath waste generation reduction of about 54 percent when the RETEC® system was in use. Implementation of the RETEC® Model SCP-6 extended the life of the anodizing bath, thus generating less chromic acid waste. However, some of this waste reduction is offset by chromic acid waste generated by the RETEC® system. The net reduction of concentrated waste generated from the chromic acid anodizing process when the purification system was in use is thus reduced to 46 percent.

Hexavalent Chromium Air Emissions. Air emissions from the DVI anodizing bath/RETEC unit were tested for hexavalent chromium. The aim of this testing was to check to see if the RETEC unit contributed to the concentration of airborne hexavalent chromium in the DVI facility. Air monitoring was conducted in both the Baseline and Operational phases of the verification test. The RETEC system exhibited a slight increase in the overall hexavalent chromium air emissions to the DVI facility. Air monitoring results indicated an average process hexavalent chromium emission increase of 0.124 µg/m3. Personal monitoring during the verification test was performed; however, the samples became contaminated with hexavalent chromium from routine paint filter change-out maintenance operations, so the results had to be discarded. Process emission readings during the operational phase of the RETEC® verification test were well within all applicable regulatory and suggested exposure limits.

Operating and Maintenance Labor. Operating and maintenance (O&M) labor requirements for the RETEC® Model SCP-6 were monitored during testing. The O&M labor requirements for the equipment were observed to be 2.8 hrs/wk. Accounting for savings in reduced labor associated with anodizing bath chemical additions, the RETEC® system O&M labor averages about 135 labor hours per year. O&M tasks performed during the

verification test included daily inspections of the unit, recording of system parameters, and additions of chromic acid flakes to the clarifier to maintain the catholyte pH below 2.

Cost Analysis. A cost analysis of the RETEC® Model SCP-6 was performed using current operating costs and historical records from DVI. The installed capital cost (1993) of the unit was $35,230 (includes $33,630 for the system and $1,600 for installation costs). The annual cost savings associated with the unit is $8,288. The projected payback period is 4.2 years.

SUMMARY

The test results show that the RETEC® Model SCP-6 does provide an environmental benefit by extending the bath life of the chromic acid anodize solution, thereby reducing the amount of liquid wastes produced by the anodizing operation without removing the required anodizing constituents of the bath. The economic benefit associated with this technology is primarily in reduced waste disposal costs associated with the life extension of the anodizing bath. Process emission increases of hexavalent chromium during the operation of the RETEC® unit are negligible. As with any technology selection, the end user must select appropriate bath maintenance equipment and chemistry for a process that can meet their associated environmental restrictions, productivity, and anodizing requirements.

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