Electrodialysis of Chromic Acid Anodizing Solutions for Bath Maintenance

An Environmental Technology Verification-Metal Finishing (ETV-MF) Pollution Prevention Center Test Report

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The ETV-MF Center conducts performance verifications of innovative, commercialready technologies designed to improve industry performance and achieve cost effective pollution prevention solutions. Test plans are developed cooperatively between Concurrent Technologies Corporation (CTC), the US Environmental Protection Agency (EPA) and the technology supplier. Verification is conducted under strict EPA quality guidelines in metal finishing shops under actual operating conditions.

This paper will present the verification test results of an electrodialysis technology for maintaining chromic acid anodizing solutions. The test methods, data analysis, and conclusions will be presented, including the environmental and economic benefits of this technology. The presentation will conclude with an update of the EPA ETV-MF Center program and the status of other verification test projects.

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VERIFICATION TEST DESCRIPTION

The electrodialysis unit was tested, under actual production conditions, on a chromic acid anodize bath solution, at an aerospace contract anodizer. Chromic acid anodizing is performed on various aluminum parts in one of two independent parts processing lines: a 27-foot or a 62-foot line. The verification test evaluated the ability of the electrodialysis unit to purify the chromic acid anodize bath solution of process contaminants in the 27foot chromic anodizing line.

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

- During the first test period (Baseline Mode), the electrodialysis 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.
- During the second test period (Operational Mode), the electrodialysis 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.

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

TECHNOLOGY DESCRIPTION

The electrodialysis system purifies and reconditions spent chromic acid by circulating it through a specialized electrochemical cell. Anodizing solution is recirculated between the anolyte section of the electrodialysis 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 the test site, saturated catholyte waste (100 gallons) from the electrodialysis unit 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.

In the Operational Mode, five weekly grab samples were collected over a six-week period from the anolyte and catholyte sections of the electrodialysis unit in addition to the samples collected during the Baseline Mode. 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 electrodialysis unit was turned on, samples were again collected. These samples are designated as "1Q" in **Table 1**, 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 system was turned on.

Average analytical results for key parameters are shown in **Table 1.** 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 operation, the purified chromic acid anodized solution maintained a relatively steady chemical and contaminant composition similar to the anodizing solution at the time of electrodialysis unit 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.

	Hexavalent	Trivalent	Total	Total	Total		
	Chromium	Chromium	Chromium	Aluminum	Magnesium		
	(by titration)	(by titration)	(by ICP-AES)	(by ICP-AES)	(by ICP-AES)		
	g/l	g/l	g/l	g/l	g/l		
Sampling week	Anolyte / Catholyte	Anolyte / Catholyte	Anolyte / Catholyte	Anolyte / Catholyte	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	N/A	N/A	52.5 / 50.5	5.4 / 7.5	0.26 / 0.31		

Titration = Standard sodium thiosulfate titration, <u>1999 Metal Finishing Guidebook</u>, 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)

Table 1. 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 electrodialysis unit is marketed as one of the beneficial conversions performed by the electrochemical process. However, as can be seen in **Table 1**, 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 the test site adds chromic acid to the anodizing bath on a regular basis, this increase in hexavalent chromium concentration cannot be definitively attributed to the electrodialysis unit's 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 2**. 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 average weekly increase of 1.053 g/l of aluminum, for an overall removal of 9,442 grams of aluminum (catholyte + clarifier overflow) from the anolyte solution over the six-week test period. Magnesium contamination was less pronounced, showing an average weekly increase of 0.0317 g/l for an overall removal of 355 grams of magnesium (catholyte + clarifier overflow) from the anolyte solution over the six-week test period. The electrodialysis unit proved to be an adequate technology for removing aluminum contamination from the chromic acid anodize solution at the test site; however, the unit was not able to completely arrest the contamination rise in the anodizing bath. Since the six-cell model tested is the smallest electrodialysis unit available, it is possible that a larger unit may solve this problem. However, since the electrodialysis 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 electrodialysis 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 2. Contaminant Removal

Energy Use. Energy requirements for operating the electrodialysis unit at the test site include electricity for the analyte 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 the test site.

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 electrodialysis system was in use. Implementation of the electrodialysis system 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 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.

Operations and Maintenance Labor. Operations and maintenance (O&M) labor requirements for the electrodialysis system 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 system 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 electrodialysis system was performed using current operating costs and historical records from the test site. 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 \$5,140. The projected payback period is 6.8 years.

SUMMARY

The test results show that the electrodialysis system 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. Unfortunately, when the labor and electrical costs associated with operating the electrodialysis system are factored in, the payback period is approximately 6.8 years. 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.