Revenue From Waste & Zero Discharge From Anodizing Plants

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Plants engaged in batch anodizing aluminum use a large number of chemicals in different process solutions. Sludge disposal is an issue, and residual ions in the discharge may interfere with compliance. Technology in use and under development that addresses these problems includes etch recovery or elimination. ion retardation to regenerate acids, potential co-products, closed-loop systems for electrocoloring, and the minimization and reuse of rinsewater. These methods are discussed in this edited version of a paper presented at the **16th AESF/EPA Pollution Preven**tion & Control Conference, held February 13-15, 1995, at Orlando, FL. The complete presentation and additional illustrations appear in the Proceedings of the conference. and can be ordered through AESF Publications Sales.

nodized aluminum has environmental advantages over alternative materials. Organic solvents are not used, avoiding VOC emissions. Polymeric materials are not involved, which allows for easy recycling of products after use. The aqueous solutions, however, result in wastes that have to be disposed of in an acceptable manner.

The Anodizing Line

Batches of extruded sections pass through a number of tanks containing aqueous solutions, each constituting a unit operation, and many followed by rinsing tanks. Typical operations include: Degrease; etch; desmut/ neutralize; anodize; electrocolor; and seal. Primary chemicals used include: Various alkalis; NaOH; HNO₃; H₂SO₄; Sn, Ni or Co salts. Intervening rinses are important to prevent unacceptable contamination of subsequent operations.

Very frequently, acid and alkaline waste solutions are collected separately and then brought together for neutralization. Following the addition of a flocculant, the solution is clarified. The supernatant is discharged to a river or sewer, and the sludge is consolidated using a filter press before transporting to landfill. The discharge is essentially a dilute solution of sodium sulfate, and the sludge is an amorphous aluminum hydroxide with 15-30 percent solids, containing trace heavy-metal hydroxides. One German plant uses expensive high-pressure tube filters, and is able to achieve almost 50 percent solids.

Origin of Potential Pollutants

Anodizing sludge is mainly composed of aluminum hydroxide, and its main source is the etching process. Figure 1 shows how the amount of sludge produced per m² of metal processed depends on the metal weight loss in the etch and sludge solids content. A typical plant may dissolve 90 g/m² in the etch. In contrast, anodizing to produce a 20 μ m film will only dissolve about 10 g/m².

A range of pollutants may be present in the clarified discharge and subject to environmental controls. Sulfate arises from the anodizing and electrocoloring solutions. Some localities limit sulfate discharge to sewers, because of the potential degradation of sewer concrete.¹ Other potential pollutants in the discharge are suspended solids caused by inadequate clarification or filtration, and trace heavy metals, which were insufficiently precipitated at the neutralization stage. Heavy metals originate from the electrocoloring process, and from nickel salt solutions used for fixing organic dyes, hydrothermal sealing or cold impregnation. The latter may also involve the use of

fluorides, while boric acid may be present in the electrocoloring solution.

Control Technology

The Etching Process Dealing with etching can be difficult because the finish it produces is critical to the market acceptance of the product.

In western Europe, the market expects a very matte finish. This is achieved using a long-life etch with a high level of dissolved aluminum held in solution by a suitable sequestrant. Typically, the solution contains 100 g/L free-sodium hydroxide and 130 g/L aluminum, and may dissolve more than 80 g/m² to give a 60° specular gloss value of 20. Using a long-life etch means the solution needs only to be dumped infrequently. The solutions are, however, very viscous, which leads to high dragout to the rinse (typically 800 mL/m²). At steady-state operation, all the dissolved aluminum becomes diluted in rinsewater and goes to the effluent treatment plant for neutralization.

In Japan, the normal product is relatively bright (60° specular gloss value of 90) and the market will tolerate the appearance of die lines. Relatively dilute etch solutions are used, typically 65 g/L free sodium hydroxide and 30 g/L aluminum without additives. Unlike long-life etch, these solutions can be recirculated through a crystallizer, which precipitates aluminum hydroxide, purifying the sodium hydroxide for reuse.² In contrast to anodizing sludge, this precipitate is relatively crystalline, has higher purity, can easily be consolidated to give 85-90 percent solids, and is salable as a raw material to the manufacturers of water treatment chemicals.³

Recovery etch systems, as used in Japan, are now also used in other parts of the world. Difficulties have arisen, however, because there seems



Fig. 1—Dependence of sludge production on etch weight loss for different sludge solids contents.



to be an international trend toward more matte finishes, which certain plants are only achieving with very high metal removal (~120 g/m²). This is higher than necessary with a longlife etch (Fig. 2).

Alternative technologies are becoming available. Mechanical etch minimizes the use of alkaline solutions. The use of wet blasting with alumina has been found to be unsuitable, because of rapid degradation of the alumina. Dry blasting with steel shot is available now.⁴ This produces a very matte, although slightly rough, finish, obscures die lines well, and is claimed to generate very little waste. It is recommended that dry blasting be followed by a brief "etch" in sodium hydroxide, which only removes a few g/m² aluminum. A French plant has installed this process.

Other processes have been developed for the recovery of etch solutions.⁵ Methods that require etch reformulation may be less attractive because of the risk that they may not be able to reproduce the finish required by the market. In other cases, it is not clear whether etch additives are recovered with the sodium hydroxide or lost into the co-product.

Ion retardation has been used extensively for the recovery of acids used in pickling solutions.⁶ This process has been extended to include alkaline etch solutions,⁷ and is being used by a plant in Spain. Sodium aluminate solution is the waste for disposal. This can be used for municipal water treatment,⁸ and has been considered in Germany to remove phosphate from municipal water to be discharged to rivers.⁹

A plant in the Netherlands is operating a process where the etch solution is regenerated by adding a silicate that precipitates zeolite A. Such technology has also been investigated in Japan for etch recovery,¹⁰ and is being used in the U.S. to regenerate extrusion die cleaning solution. Zeolite A has application as a builder for phosphate-free detergents and as a desiccant.

A method used in Switzerland involves the precipitation of crystalline aluminum hydroxide in the etch tank.¹¹ The solution is recirculated through a filter to remove the precipitate. It is claimed that a chemical equilibrium is established between the solute species and the solid material.

A membrane process, diffusion dialysis, has been proposed to remove sodium hydroxide from the solution for return to the etch tank.¹² The etch solution is passed across one side of an ion exchange membrane, while water flows across the other side. Sodium ions pass through the membrane to produce the regenerated stream, leaving a sodium aluminate solution that goes to a crystallizer, yielding further purified sodium hydroxide and an aluminum hydroxide co-product.

Reaction of spent etch solution with lime allows caustic recovery, and generates an aluminate that may be used as a cement additive.⁵

The Anodizing Process

Anodizing solutions must be dumped regularly when the dissolved aluminum reaches an unacceptable level (20 g/L, although some plants may adopt a much lower maximum).

Diffusion dialysis is used in Japan to control the level of aluminum in the anodizing solution.³ Sulfate ions pass across the membrane, producing regenerated acid. The waste is a dilute aluminum sulfate that, although of little value, may be used in the production of alum for water treatment. There have been problems with this technology, because the fragile membranes have tended to foul, and manual cleaning is expensive.

Many plants are using ion retardation.⁶ It also produces a dilute aluminum sulfate waste. The process involves an ion exchange resin that physically retards the transfer of acid through the column, allowing salts to be transmitted relatively unimpeded. Subsequently, the column may be regenerated using water to produce acid of similar concentration to the free acid in the original solution.

Table 1 Performance of Ion Retardation & Diffusion Dialysis For Acid Recovery

Stream Spent acid	Ion Retardation 184 g/L H ₂ SO ₄ 12.2 g/L AI	Diffusion Dialysis 170 g/L H ₂ SO ₄ 20 g/L Al
Recovered Acid	175 g/L H ₂ SO ₄ 4.2 g/L Al	120 g/L H ₂ SO ₄ 0.5 g/L Al
Waste	13 g/L H ₂ SO ₄ 12 g/L Al	50 g/L H ₂ SO ₄ 19.5 g/L Al

Table 1 gives examples, comparing the performance of diffusion dialysis and ion retardation, indicating that ion retardation has higher acid recovery. Both processes are effective at controlling the aluminum concentration in the anodizing bath.

Electrocoloring Solutions

Tin, nickel and cobalt salt solutions are used worldwide to produce bronze and black finishes. Because of their light adsorption characteristics, however, deposits of each metal produce bronzes of slightly different hue. This difference is generally sufficient for customers not to want mixed products. Consequently, regional and national differences have arisen concerning electrocoloring solutions. Nickel is used almost exclusively in Japan, while tin predominates in Europe. The use of cobalt is declining in favor of tin because of the cost of cobalt salts and their environmental impact in effluents.



Fig. 3—Schematic diagram for nickel sulfate recovery.

Technology exists for closed-loop systems that effectively eliminate certain heavy metal salts of electrocoloring baths from the effluent treatment system. In Japan, rinsewater from counter-flowed rinse tanks following the electrocoloring bath is concentrated by reverse osmosis and the concentrate is returned to electrocoloring solution (Fig. 3).¹³ Impurities that accumulate in this solution, sulfate and sodium, are removed by ion exchange. Because of the chemical similarities between nickel and cobalt, it is anticipated that such a system would be equally effective for cobalt-based solutions.

Alternatively, nickel or cobalt can be removed from rinsewater using ion exchange, and then returned to the electrocoloring solution.³

Closed-loop tin recovery can be more difficult. Because tin electrocoloring solutions are quite acidic, reverse osmosis membranes that have limited acid resistance may be unsuitable. What is more important, tin electrocoloring solutions tend to precipitate stannic hydroxide during use, which cannot easily be regenerated to the stannous ion needed for electrodeposition. Recirculating systems are under development in which the hydroxide can be removed in a form amenable to consolidation into a high-solids sludge. This material has potential value as a raw

material for the inorganic chemicals industry.

Sealing Solutions

Different standards have influenced the development of sealing technology in different parts of the world. Japan makes extensive use of electrodeposited lacquers to seal anodic films, possibly because of tight standards on the alkaline resistance of anodized finishes.² European standards have stressed the importance of admittance tests. Consequently, boiling-water sealing for long times is favored. Different accelerated tests have been emphasized by North American standards, making the adoption of cold impregnation techniques easier.14

The effectiveness of cold impregnation techniques depends on maintaining bath contamination below certain levels (Table 2),¹⁴ which determines the solution lifetime. The presence of fluorides and heavy metals in the formulations may cause environmental difficulties on disposal. Such considerations have to be offset against the energy savings associated with these processes in comparison with boiling-water sealing.

Boiling water seals need to be dumped regularly, because of the buildup of colloidal aluminum hydroxide that sticks to, and adversely affects, the appearance of the work, and the accumulation of sulfate, which will affect sealing quality. The maximum concentration for sulfate is often taken to be 250 mg/L. The contamination level, however, is sufficiently low and environmental problems are unlikely.

Water Consumption

The main use for water is rinsing. There are opportunities to eliminate rinses, and to minimize water consumption.

Degreaser formulations are available that are compatible with the etch

Table 2 Limits on Contaminants In Cold Impregnation Solutions

Contaminant	Limit (mg/L)
Phosphate	5
Aluminum	250
Sodium or Potassium	300
Ammonium	1500

so that no intervening rinse is necessary. Similarly, if sulfuric acid (preferably spent anodizing solution) can be used in place of nitric acid for the desmut, then there is no need for a rinse following the operation. Also, if a nickel-free hydrothermal seal is

Table 3 Technologies for Desalinated Water

Technology	Regime Of Lowest Operating Cost (g/L)	Water Purity
Evaporation Reverse osmosis Electrodialysis	>100 10–100 0.5–10	Very high High Low Medium

used, it has a low level of contamination and may be further employed as rinsewater, particularly after being passed through a heat exchanger system.

Counterflow rinses, static rinses, spray rinse systems and adequate drainage practices are frequently used to minimize rinsewater consumption and carry-over. Typically, horizontal lines consume water at about 40 L/m², while the value may be reduced to half in a vertical line.

Generally, spray rinse systems are installed above a process tank to wash loads and flight bar systems on withdrawal from the tank and reduce carry-over, or over a conventional rinse tank to reduce water consumption associated with the rinsing operation. One Dutch anodizer, however, is relying on spray rinsing over an empty tank. This method is expected to significantly reduce water usage. Static rinses are useful to reduce the carry-over into counterflowed rinses, which enables reductions in volumetric flow rate. Also, feeding the static rinse back to the process solution partly counteracts losses caused by dragout.

For the reuse of rinsewater, it is necessary to concentrate the solutions so they may be returned to the process tanks. This assumes that the process solutions have recovery systems that enable aluminum to be removed. If the water generated by the concentration process is sufficiently pure, it may be reused for further rinsing. Technologies potentially appropriate for concentration are evaporation, electrodialysis, reverse osmosis and ion exchange.

Experience with desalination systems determines which methods have the lowest operating costs for particular solution concentrations (Table 3¹⁵). This suggests that anodizing rinsewater containing 10 g/L total sulfate should be concentrated using electrodialysis or reverse osmosis,

while etch rinsewater with 20 g/L total sodium hydroxide be processed by reverse osmosis. Other factors, however, have to be considered. The ability of the technique to produce a concentrated stream must be evaluated. For example, there are currently technical limitations with reverse osmosis membranes for either highly acidic or highly basic streams because of membrane stability. This probably excludes them from concentrating etch and anodizer rinsewaters to process concentrations. Cation exchange electrodialysis membranes are not well developed, making them unsuitable for concentrating etch rinsewater. Electrodialysis is probably the most appropriate technology for concentrating anodizing rinsewater, while evaporation is preferred for etch rinsewater.

Eliminating rinses or reducing their water consumption requires an understanding of the effect of carryover on the product quality produced by subsequent operations. Mass balance analyses show how contaminants may build up to a steady-state level. For instance, modifying rinsing after anodizing is subject to certain requirements. The first rinse should be sufficiently acid (<pH 3.0) to ensure adequate removal of dissolved aluminum from within the pores that, otherwise, may precipitate and subsequently affect the uniformity of electrocoloring or organic dyeing. If the last rinse is too acid, carry-over



Fig. 4—Advantage of counterflow rinsing over parallel rinsing.

Fig. 5—Rinse tank concentration vs. rinsewater flow rate (counterflow).

will progressively acidify the coloring bath and affect its operation. Acidic tin electrocoloring baths are more tolerant of acid carry-over than neutral cobalt baths. Steady-state mass balance analyses show the advantage of counterflow rinsing over parallel rinsing, where each rinse tank has its own feed and effluent going to waste. Consider the following parameters:

- Rinse time per tank: 3 min;
- Loads per hour: 2;
- Tank volume: 40 m³;
- Drag-in per load: 80 L;
- Area per load: 175 m²;
- Process solution: 275 g/L.

The improvement in rinsing, based on the concentration in the last rinse, increases with rinsewater flow rate and more dramatically as the number of rinses increases (Fig. 4). For the counterflow rinse system with three tanks, the steady-state concentration depends on the rinsewater flow rate (Fig. 5). In this case, effective rinsing is achieved with a flow rate of about 1.2 L/m² load area. In practice, a number of process tanks would be feeding loads into the same rinse system, which would increase the rinsing requirements. If a line contains three etches and three anodizing tanks, this analysis suggests that it should be feasible to operate with a rinsewater flow of less than 10 L/m².

Such analyses, however, provide no information about the time to achieve steady-state concentrations. Figure 6 shows how the concentrations in the rinse tanks increase with time. With a rinse flow rate of 1000 L/hr, steadystate concentrations are approached after about 150 hr operating time. The rinsewater flow is assumed to be constant over that time. This analysis indicates that, assuming no perturbations, a number of weeks may elapse before steady-state conditions are achieved. It is also interesting to compare Figs. 5 and 6. For a rinsewater flow rate of 2.8 L/m² (1000 L/hr), Figure 5 indicates that the first rinse will have a steady-state concentration of about 41 g/L, while Figure 6 shows a higher value of about 52 g/L. It is believed that relying solely on steady-state mass balance analyses may underestimate rinsing requirements.

Drag-out is the most important factor governing rinsing requirements. With optimum draining practices, this depends on solution viscosity, which in turn is controlled by solution temperature and concentration. In a rinse system, the solution concentration, and most likely the temperature, will vary in the rinse tanks during the time before steady-state is achieved. This means that drag-out will vary. Figure 7 indicates the effect of assuming that drag-out is constant with time. A linear relationship with solution concentration was used to determine the instantaneous drag-out,

and the results were used in comparison with a fixed drag-out of 450 mL/ m². This shows that the concentration in the final rinse may be too high by a factor in excess of three, if it is assumed that drag-out does not vary.

Revenue From Waste

End-of-pipe waste treatment can be a cost for which there is no return on the investment. Regeneration systems are preferred because they involve a saving in the cost of chemicals. In order to get an even better return on investment, the waste should be a source of revenue. This can be achieved by producing potentially salable co-products (Table 4). The ability to sell particular co-products, however, depends on local opportunities and the presence of impurities.

With unstable, low value or hazardous co-products, transportation distance and the related costs, it is best to have a local customer. Sodium aluminate, for example, may be insufficiently stable to allow long transportation distances. High transportation costs may be associated with waste solutions and anodizing sludge with its high water content.

Impurities may also be critical to marketability. This is particularly true for the manufacturers of water treatment chemicals used for potable water. Co-products from etch recovery systems have the highest purity because they are contaminated with only alloying constituents. Nevertheless, these may be at a higher level

Time (h) Rinswater flow rate (L/m²)

Fig. 6—Time history of concentrations in a three-tank countercurrent rinse.

Fig. 7—Effect of drag-out assumption on final rinse tank concentration.

than in the raw materials conventionally used. This does not necessarily preclude anodizing line co-products from all water treatment applications. It is important to determine whether the application really requires a highpurity product, or whether the purity level is an inherent feature of the conventional raw material. For example, alumina has a high purity because this is a characteristic of the Bayer process.

Certain cements are sensitive to the presence of sodium or sulfate. Industrial ceramics and refractories are expected to be white; the presence of heavy metals may impart color.

Many anodizers are successfully selling their wastes as co-products. One Italian anodizer has an alum plant next door. Co-products require the same considerations as main-line products in quality and consistency.

Implementation

Because a waste treatment plant can represent a significant cost, planning for incremental installation is important. Actions should stage developments through the generation of revenue from waste toward "zero discharge" operation. Zero discharge operation may never be needed, although at least one Japanese anodizer already has to meet that requirement. Technology planning toward that goal ensures that no equipment is installed that later suffers unplanned redundancy. Each plant has to develop its own plans based on its own circumstances. This depends on the facilities being used, and particularly on local opportunities to sell potential co-products.

Initial actions should be aimed at reducing rinsewater flow rates. Subsequently, recovery systems may be introduced to eliminate heavy metal-containing effluent. The installation of etch recovery is costeffective, but requires careful consideration of product requirements and means to dispose of waste acid. It spreads capital expenditure if an acid recovery system can be introduced later. The final stages to achieve zero discharge involve reuse of rinsewater. Here, mass balance analyses are important to understand how impurities may build up, and avoid unacceptable contamination of process solutions. It is particularly important to control sodium contamination of electrocoloring baths that may be

Table 4Applications of Potential Co-products from Anodizing Lines

Co-product Anodizing sludge	Application Cement Water treatment chemicals Absorbents
Etch recovery sludge	Water treatment chemicals Firebricks Ceramics Fire retardants
Sodium aluminate	Water treatment
Zeolite A	Washing powders Desiccants
Spent anodizing acid	Waste neutralization
Dilute $Al_2 (SO_4)_3$	Water treatment chemicals
8% alum	Water treatment
Tin hydroxide sludge	Fire retardants

achieved using an ion exchange unit. Similarly, the accumulation of acid in neutral pH electrocoloring baths should be investigated.

Conclusions

1. Environmental technology is available for anodizing plants to produce salable co-products from waste and institute zero discharge operation. This includes recovery systems for etch, anodizing and electrocoloring solutions.

2. A technology plan is important to stage implementation in a logical

manner without building-in redundancy. Developments for each plant will depend on its local circumstances regarding environmental legislation and opportunities to sell co-products.

3. National standards and markets have led to diverse products internationally, which in some cases inhibit the implementation of the best environmental technology. Examples relate to etching, electrocoloring and sealing.

4. An important element of any technology plan is the selection of the most appropriate etching technology

to satisfy market needs and long-term environmental requirements.

5. Mass balance analyses are important tools in developing a technology plan, particularly in determining how impurities will accumulate in a complex recycling system.

Acknowledgments

The authors thank the management of Alcan International, Ltd. for permission to publish this work, and also acknowledge colleagues in Alcan and NLM, whose comments and experience have been invaluable.

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