

RECOVERY OF PHOSPHORIC ACID USED IN THE BRIGHT DIP FINISHING OF ALUMINUM

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1.0 Phosphoric acid based aluminum Bright Dips

The R5 process combines concentrated (65-80% w/w) phosphoric acid, with small amounts of nitric acid, di-ammonium phosphate and copper, to chemically polish aluminum parts prior to sulfuric acid anodizing. Removal of metal from the part's surface causes aluminum phosphate to accumulate in the acid but the level usually stabilizes in the 30 - 45 g/L (as aluminum) range. Higher levels require the addition of sulfuric acid to prevent transfer etch or the formation of aluminum phosphate crystals ("ice") in the bath. Excessive build-up is rarely a problem however, as the high dragout rate of these viscous solutions provides a natural purge for the dissolved aluminum.

The dragout leads to a substantial loss of bright dip solution and bath replenishment is one of the largest expenses an aluminum finisher has. To reduce this expense, most plants operate a counter-current rinse system to generate a 35% w/w co-product which can be sold to fertilizer manufacturers. Up to 20% of the acid cost can be recovered this way. Co-product cannot be recycled directly back to the bright dip, however. This would close the loop on the aluminum build-up and quickly "ice-up" the bath.

Cation exchange can be utilized to remove aluminum from the rinsewater. In the mid 1970's, a number of conventional and moving bed ion exchange systems were installed for bright dip recovery. None of these systems were used for any length of time, however, due to a number of problems:

- excessive sulfuric acid regenerant usage led to impractical neutralization and waste disposal expenses,
- dilution of the phosphoric acid and high evaporation costs,
- mechanical problems, resin degradation and large physical size.

The reciprocating flow ion exchange or "RECOFLO" process has been used effectively and economically for the recovery of phosphoric bright dip solutions since 1980. Through its use of fine mesh resins, counter-current regeneration, and low exchange loadings, this patented technique has overcome the problems associated with other ion exchange systems on this application.

2.0 The Recovery Process

2.1 Rinse capture

The general arrangement of the system is shown in Fig. 1. The bright dip bath is followed by at least two, and preferably three, recovery rinses. Three counter-flow rinses capture approximately 95% of the phosphate carried out of the bright dip tank. To minimize phosphate carry-over, a free flowing rinse should be used immediately prior to the anodizing tank.

Rinsewater is recirculated between the first recovery rinse, RR1, and a rinse feed tank/filter until the phosphoric acid reaches a preset level in the 10 - 20% w/w range. Then the cation exchange process begins. During its cycle the cation exchanger, or DCU, uses condensate water from the evaporator to rinse trace amounts of phosphate out of the ion exchange column. This water is sent to the final recovery rinse, RR3, on the finishing line. By reusing the condensate, waste and evaporative loads are reduced.

The media filter (right) is used to remove any particulate material from the rinse water prior to cation exchange.

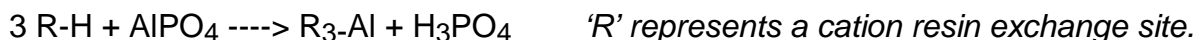
The main control panel (center) uses a central PLC and graphic display of system status.

Remote I/O (input/output) modules interface with the central panel, providing control for the cation exchanger (left).



2.2 Cation exchange of rinsewater

The cation exchanger, or DCU, converts aluminum phosphate into phosphoric acid. Rinse solution, containing phosphoric acid, aluminum phosphate, etc., is pumped from a feed tank into the bottom of the resin column. Aluminum and other cationic metals such as copper are removed by the cation exchange resin, as the rinsewater flows up through the column. The chemical equation shows the process that takes place during the loading step.



After the resin has been loaded with aluminum, condensed water from the evaporator is pumped through the column, rinsing phosphoric solution back into the feed tank. Extra

water is used to ensure that as little phosphate as possible is left in the column. This wash water is returned to the final bright dip rinse, RR3, as previously mentioned.

Sulfuric acid regenerant is pumped into the column to regenerate the resin as shown in the equation below. A heavy dose of sulfuric acid is required because the tri-valent aluminum bonds strongly to the resin.

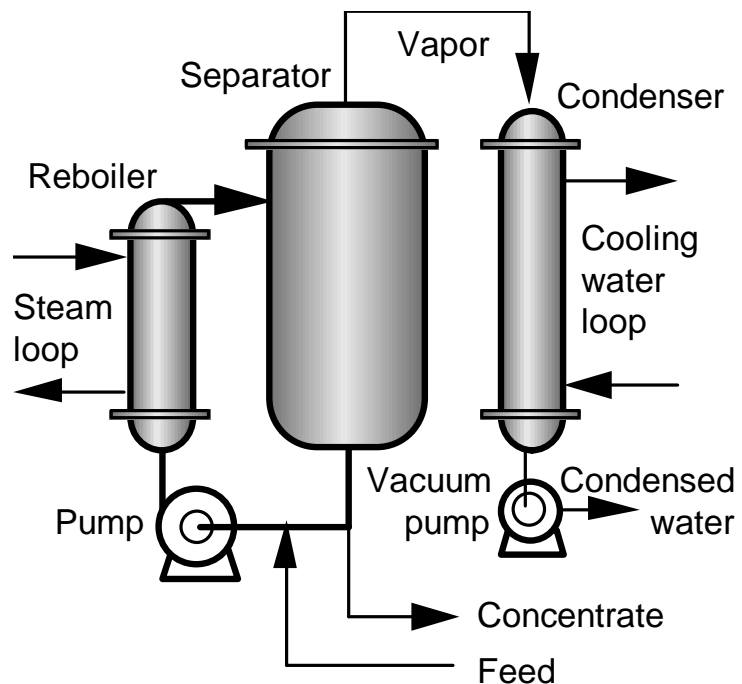


Water is used to rinse the regenerant from the column. The rinse is split into weak (waste) and strong (recoverable) fractions.

2.3 Concentration of purified rinsewater

Purified rinse water must be concentrated to 80% w/w to be reused in the bright dip tank. The evaporator used is a forced circulation vacuum unit consisting of a steam heated shell and tube reboiler, separator, circulating pump, vacuum pump, a water-cooled shell and tube condenser and cooling tower.

During the evaporative cycle, phosphoric acid is pumped from the separator into the bottom of the reboiler where it is heated inside the tubes to the boiling point. The boiling liquid leaving the reboiler enters the side of the separator. The water vapor passes through a demister pad at the top of the separator, before continuing over to the condenser.

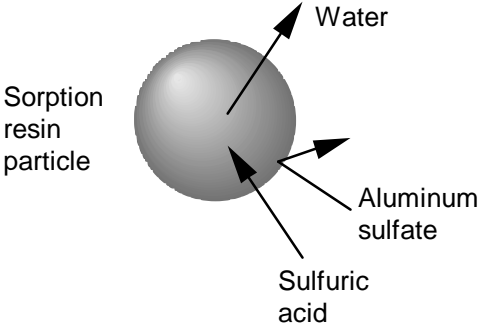


Vapor condenses inside the tubes of the condenser, collecting in a receiving chamber in the bottom section of the unit. A vacuum pump removes any non-condensable gases present (i.e., air), maintains a vacuum and removes condensed water from the evaporator. The condensate is used in the DCU for rinsing. Cooling water is circulated through an outdoor cooling tower.

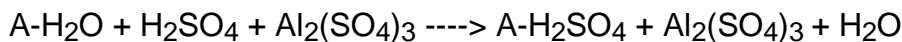
2.4 Reuse of acid regenerant

The cation exchange process must use an excess amount of sulfuric acid in order to remove the aluminum from the resin. This is a particular problem with aluminum due to its trivalent nature. Previous attempts to recover bright dip rinse by cation exchange have had a problem with this. The costs of neutralization and waste disposal counter-balanced the savings in phosphoric acid.

Since 1976, RECOFLO acid sorption technology has been used to remove dissolved metals from mineral acids. One of the largest applications has been the purification of sulfuric anodizing solutions. One of the keys to the success of the RECOFLO phosphoric recovery system was the use of an acid purification unit (APU) to reclaim the residual sulfuric acid from the concentrated DCU waste.

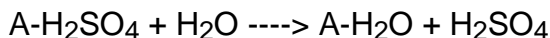
<p><i>Sorption resin technology employs specially treated ion exchange resins that have the ability to sorb free (unused) mineral acids while rejecting the salts (e.g., aluminum sulfate) of these acids. The most unique feature of these resins is their ability to release the acid with a simple water wash.</i></p>	
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During the loading step, acid solution (strong DCU regenerant rinse) is pumped into the column. Utilizing acid sorption, the APU retains free sulfuric acid and rejects aluminum sulfate.



'A' represents a sorption resin site.

After the water in the column from the previous cycle is displaced, the deacidified aluminum sulfate byproduct solution is collected. Water is then pumped through the column to extract the acid as shown below.



After the acid feed solution from the loading step is displaced from the column, a purified acid product is collected. The total APU cycle takes about 5 minutes. The purified acid is fortified with fresh 93% sulfuric and reused as DCU regenerant.

3.0 Field Installations

The first RECOFLO phosphoric recovery system was commissioned in Japan at the Kyoritsu Alumi Co. Ltd. in March 1980. Kyoritsu was subject to severe limits on phosphorus as the plant effluent was discharged directly to a lake. This was also a challenging application as the electro-polishing bath was formulated with equal volumes of concentrated sulfuric and phosphoric acids.

The high boiling point and corrosive nature of the mixture required special operating conditions for the DCU and a unique two-stage evaporator design. A primary forced circulation vacuum evaporator brought the solution to 60% w/w and was followed by a secondary hot-oil fired glass-lined steel "kettle". Despite the difficult design conditions, the system has experienced no major problems since startup. The original resin was replaced after eight years of service and the system has seen only minor reductions in operating efficiency.

This phosphoric acid recovery system was designed to recover over 2000 tons of 80% acid per year. The vacuum evaporator is located on the right side. To the left are the DCU and APU. The cooling tower was roof mounted. The total area required for this system was 2000 square feet.



All other bright dip installations have been in the U.S., mostly larger plants using R5 (80% phosphoric acid) formulations.

Location	Plant	Installed	Status
1. Georgia	Extrusions	1982	Operating
2. Ohio	Extrusions	1983	Operating
3. Michigan	Sheet	1985	Operating
4. Georgia	Extrusions	1987	Operating
5. Kentucky	Extrusions	1987	Operating
6. Illinois	Sheet	1988	Operating
7. Kentucky	Formed parts	1990	Plant closed - see (8)
8. Arkansas	Extrusions	1994	Operating
9. Michigan	Sheet	1995	Operating

10. Ohio Stampings 1995 Being installed

Several other systems have been used by the lithoplate industry to purify and recycle phosphoric anodizing solutions. To date, no systems have been installed in Europe or at smaller (less than 500 tons per year 80% phosphoric acid usage) American plants. There are number of reasons for this.

- European plants doing bright dip tend to be much smaller (typically consuming 80-90% less acid than a large U.S. plant).
- European chemistry frequently involves the use of proprietary organic additives, making the recovered solutions difficult to reformulate. Also, high sulfuric acid levels are used.
- The cost has also been affected by the evaporator materials required for the high sulfuric content often found in European bright dip solutions.
- The system design has not been geared to the smaller user.

The above considerations has led to the development of a number of process improvements.

4.0 Process improvements

The size of the equipment required at larger installations requires separate cation exchange (DCU) and acid sorption (APU) skids. Tanks and pumps are needed to transfer liquids between units and a significant degree of field erection is involved. While practical for large plants, this arrangement may not be economical for plants consuming less than 500 tons per year of 80% acid. A number of design changes have been made to develop a system geared to these plants.

4.1 Integrated DPU System

An integrated cation exchange / acid sorption system, which has been used successfully to purify hydrochloric acid in the lithoplate industry has been adapted for bright dip recovery.

The integrated DPU system fixes both resin columns on one frame, however, the real advantages of this design relate to the coupling of the liquid flows. For example, when the cation exchange column is regenerating, the acid waste flows directly through the acid sorption column. Acid sorption is more efficient because the acid content in the regenerant stream gradually increases and decreases through the regeneration cycle. This "profile" cannot be obtained when an intermediate storage tank is used because of the intermixing that occurs. Improving the sorption efficiency, reduces the amount of sulfuric acid regenerant that is lost and waste neutralization requirements.

Aside from the improved chemical process results, using the DPU eliminates some of the tanks and pumps that were needed for separate units, and a significant amount of field piping.

Typical DPU Results	Total H ₃ PO ₄ (g/L)	Al (g/L)
Bright dip bath	1300	40
First rinse, RR1	280	8.3
Product from DPU	252	1.2
Waste from DPU*	40	18.6
Product from evaporator	1300	6.0

* Combined waste from the cation exchange and acid sorption processes - will also contain 55 g/L of free sulfuric acid.

4.2 Evaporator

For smaller systems the heat transfer advantages of a forced circulation evaporator must be weighed against the increased cost (both capital and installation) of this design. For smaller systems the natural circulation method works well and costs less. An added advantage is that the unit can be pre-assembled to a greater degree, reducing the cost and time required for installation and start-up.

5.0 DPU System Economics

Installed cost savings of phosphoric acid recovery systems are derived primarily from the reduced acid purchases. There is also a credit for the amount of caustic soda (or other neutralizing agent) that is required to treat the phosphate that is not captured as co-product. The table on the following page outlines a sample case with a design basis being an annual phosphoric acid usage of 400 tons 80% and a recovered co-product volume being 731 tons 35%.

6.0 Summary

The RECOFLO phosphoric acid recovery has been established as a reliable and economical alternative to selling 35% co-product. The efficient design of the system recycles internal rinsing streams to reduce water consumption, steam requirements and waste flow.

The system can handle the high sulfuric acid content of certain proprietary and electropolishing formulations through the use of specially developed cation exchange operating conditions and resistant materials of construction in the evaporator.

Recent improvements have made the system much more economical for plants consuming under 500 tons per year of acid. The use of an integrated DPU not only reduces the equipment cost, but improves chemical performance as well. A natural recirculation evaporator is a simpler design that trades off heat exchange efficiency for reduced capital and installation costs.

