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INDUSTRIAL PROCESS DESIGN FOR POLLUTION CONTROL

ACID REGENERATION AND METAL RECOVERY IN THE METAL FINISHING INDUSTRY

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WATER POLLUTION CAN BE REDUCED
BY PROCESS MODIFICATION:

Acid Regeneration and Metal Recovery
in the Metal Finishing Industry

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Various acid and alkaline etching and cleaning processes are being used by metal finishers to remove surface oxides, scale, and in general, prepare the metal surface for its intended use. After the process solution has gained a certain concentration of a metal which is being dissolved, the metal dissolution rate is reduced and the processing solution is normally discarded. Dumping of these used processing solutions entails loss of chemicals and generation of metal hydroxide sludge. The original chemicals and treatment chemicals are costly, but the greatest cost appears to lie in sludge concentration, drying, and disposal. Many areas in the country are seriously objecting to metal hydroxide sludge disposal.

The regeneration of the processing solution is most often far more economical than dumping. The regeneration and metal recovery system best suited, will depend on the nature of the processing solution and the metal to be recovered. Practical applications are in use for each of the recovery processes discussed: (a) crystallization; (b) electrolytic metal removal; (c) precipitation; (d) electrodialysis; and (e) ion exchange. Examples of various applications are given.

Pollution-abatement-connected expenditures are continually increasing. Solid waste handling is perhaps the most expensive part of waste treatment. Precipitated metal salts provide extremely bulky, mainly water-content sludges. There is also great concern regarding where these sludges may be disposed of in view of potential resolubilization, ground water contamination, or the washdown of the sludges into the river courses. The volume of dissolved metal solids is so great, and the volume of sludges generated is so enormous, that the general concern is justified. Space for the deposition of these sludges in most areas will not be available.

As an example, we may cite that one pound of dissolved aluminum can create 150 lb. of treated metal sludge. Precipitated metal salts provide extremely bulky, mainly water-content sludges. Experience indicates that finishing of aluminum extrusions will result in the dissolution of approximately 1.5% of the metal processed. From these premises, it may be calculated that the processing of each 100,000 lb. of aluminum will yield in the average 225,000 lb. of sludge.

An exhausted processing solution usually contains high concentrations of dissolved metal salts. While the metal solids remain as sludges, the discharged liquid waste, after neutralization, contains the anions according to the original chemical make-up. The dissolved salt content of these wastes is a serious concern. This especially is true as far as nitrates and ammonia are concerned, in view of the nutrient content. Chlorides and sulfate may impair the usefulness of the watercourse for drinking water downstream.

Logic of deliberation

When selecting metal finishing processes, one should weigh carefully opportunities for regeneration of the processing solution, avoiding dumping and new solution make-up, while at the same time paving the way for the recovery of the metals that were originally dissolved. Judging the value of the various processes available from this standpoint will lead to new logic of deliberation, considering as the total cost of processing also waste treatment versus regeneration and recovery.

The greatest difficulty encountered when recommendations are made for process changes, aiming for regeneration or metal recovery, is usually the reluctance of the processing people for any change. This to some extent is due to the split responsibilities between cost control for processing and waste treatment. Operating responsibilities are also divided, and finally, there is the black magic that is even today part of almost every metal finishing process.

One of the most important aspects of metal processing solution regeneration and metal recovery, besides the obvious value of by-product recovery and avoidance of waste treatment and sludge generation, is the fact that the process can be conducted at a uniform concentration level, avoiding the filling of the tanks with a new process solution, operating this through a number of processing cycles until the efficiency falls to the extent that the decision for dumping is made, and a new process solution is prepared. Most of these processes are conducted without laboratory assistance and generally are based on experience factors—so many batches, so many days, indicating the anticipated reduction in performance leading to a dump. That the process solution could not perform equally well if it is operated for five days, and that there may be a significant difference between the performance of the first
and the fifth day, and that there is further wastage if a certain percentage of the work does not meet standards on the fifth day, is obvious.

In the following, I will discuss a number of practical applications that are in use to effect the regeneration of the processing solution and metal recovery in the course of the regeneration steps:

**Crystallization**

Operating the process near saturation of the soluble metal content at an elevated temperature, recirculating part of the treatment solution, cooling the recirculated process solution, and removing the metal salt crystals before returning the regenerant is practiced in many processes. Many of the iron pickling processing solutions remove ferrous sulfate from the iron pickling solution in this manner. The pickling solution, as it is recirculated, is enriched with sulfuric acid to replenish the consumed acid, and since iron sulfate is less soluble in the higher concentration acid solution, both at lower temperature than that at which the process is conducted, or at a high temperature, near boiling, the regeneration may take place on either end of the scale. When cooling ferrous sulfate, heptahydrate is removed. When heating the acid solution, the ferrous sulfate monohydrate is gained.

Another typical example is copper etching with ammonium persulfate, in which case the ammonium persulfate etch solution is cooled to remove the copper ammonium sulfate which becomes over-saturated at a reduced temperature, returning the regenerant and replenishing the consumed ammonium persulfate.

A recent development is copper and cuprous alloy pickling with sulfuric acid solution containing hydrogen peroxide and stabilizing agents. The process will work equally well near saturation since the oxidizing ability of the hydrogen peroxide is not affected by the fact that the acid solution may be close to saturation in the metals to be dissolved. To avoid crystallization of the metal salts on the work in process, the solution is recirculated into a crystallization tank where, with some cooling, the cupric sulfate crystals fall out and the acid solution with the hydrogen peroxide content is returned to the process for further pickling. Some of the sulfuric acid is lost when cupric sulfate is removed from the system, thereby requiring periodic addition of sulfuric acid, unless the cupric sulfate itself is recovered electrolytically in the form of metallic copper and sulfuric acid.

**Electrolytic Metal Removal**

Electrolytic metal removal from acid pickling solutions has been practiced for many years in copper and cuprous alloy processing plants. The copper is dissolved in the pickling operation, cupric sulfate is formed, and as the cupric sulfate increases in the acid solution, a stream is continually recirculated through an electrolytic recovery system where the copper is recovered in the metallic form and the acid is again released for further processing.

A recent very ingenious, proprietary process, developed and used by Western Electric for printed circuit etching, employs a cupric chloride solution which is continuously regenerated electrolytically. In this process, cupric chloride is sprayed on the copper foil to dissolve the unwanted areas. During the process, cupric chloride is reduced to the cuprous form and additional copper is dissolved as cupric chloride. In the electrolytic system, diaphragms separate the anode and cathode compartments and the oxidizing electrode reaction in the anode compartment reoxidizes the cuprous chloride to the cupric state for regeneration of the cupric chloride etchant, while at the same time, in the cathode compartment copper is plated out in powder form on metal cathodes. The metal cathodes are continuously moved out of the cathode compartment and are conveyed through a high-pressure water spray which removes the copper powder that is not entirely adherent. The copper powder is collected and sold as a by-product. The hydrochloric acid that was bound with the copper at the same time is released again in the form of free hydrochloric acid to provide a regenerated solution to continuously be useful as an etchant.

**Precipitation**

Many chemical reactions will slow down when the metal content reaches the saturation level. Acid cleaning or etching will stop. This is not the case, on the other hand, when an external force continuously provides the necessary energy for continued metal attack. Earlier we mentioned the effect of hydrogen peroxide addition to an acid solution, but even more so is this the case with electrolytic pickling, etching, machining, and electropolishing systems. All these processes are operated at a solution concentration where either the metal salt is near saturation, and therefore becomes insoluble when additional metal salt is dissolved, or the solution itself is neutral and therefore leading to precipitation of the dissolved metal ion. Many of the electrolytic stripping solutions are so formulated that they are operated at saturation of metal content. Electropolishing solutions have a high acid content, again leading to low solubility for the metal salts. Most of the electrochemical machining processes use neutral salt solutions in which the metals precipitate as insoluble ions. All these solutions require no regeneration because they are self regenerating. The precipitated metal sludges have to be removed periodically to avoid accumulation, and these metal sludges then can be recovered.

**Electrodialysis**

Electrodialysis should open up many similar applications because the metal salt can be easily passed through the cation membrane and is available for electrolytic removal or precipitation, while the anolyte compartment contains the acid solution ready for recirculation back into the process. With chromic acid etch or pickling systems, the anode reaction allows the regeneration of the trivalent chromium by reoxidizing it to the hexavalent state.

An example of a useful application is the regeneration of chromic-acid-type etch solutions for printed circuit manufacturing. The processing solution gains continuously in copper, and some of the hexavalent chromium is reduced to
the trivalent form. For the most efficient continuous process, the copper content should be held at an optimum level to ensure uniform etching rates, and the trivalent chromium should be reoxidized to the hexavalent form to provide the active etchant. To avoid building up copper on a cathode in the closed electrodialysis cell, the copper is electrolytically recovered in an external electrolytic recovery cell, the catholyte solution being recirculated from the catholyte compartment to the external cell and back. The chromic acid etchant, on the other hand, is returned to the etching process for further copper removal.

**Ion exchange**

In view of the high concentration of metal salts that normally are encountered and have to be removed in a continuous manner, the fixed bed ion exchange installations are not as useful as are the moving bed ion exchange columns. A typical example for a process such as this would be the removal of aluminum from a high-concentration phosphoric acid solution used in the bright dipping of aluminum. The aluminum is retained in the cation exchanger and as the resin in the column is pulsing to the regeneration phase, sulfuric acid solution regenerates the resin, providing a waste of aluminum sulfate with some wash waters containing the residue of the sulfuric acid used for regeneration. The phosphoric acid freed of the aluminum content is returned to the process for further use.

Another system using ion exchange resins, but actually not truly an ion exchange system, was developed recently where the ion exchange resin is employed as an adsorption medium. The design of the Lancy closed-loop contactor is a continuous pulsed ion exchange resin column in which the acid solution and metal separation is achieved by utilizing the acid adsorbing capabilities of the resin. Similar results for other types of solution could be achieved by using other adsorbing media, or with other processing solutions. The process recently revealed separates phosphoric acid solution used in aluminum processing from the aluminum phosphate salt it also contains. The ion exchange resin is pulsed and thereby moved from the loading zone and in a closed loop back to the loading again. The pulse water and counter-pulse water are closely controlled to avoid disturbing the interface of the solution to be regenerated. As a typical example, 30% phosphoric acid solution containing 20 g./l. aluminum is regenerated, providing a product stream containing 28% phosphoric acid and 1 to 1½ g./l. aluminum, and a waste stream containing 18 g./l. aluminum and only 50 g./l. phosphoric acid. For pulsing and stripping, only water is used, with most of the pulse water and regenerant being recirculated. In view of the fact that no chemicals are required for regeneration, and that the water consumption is very low, the economics of the system appear very attractive.

**A multitude of opportunities**

In this listing of processes available today, we are not aiming for an exhaustive survey of the field; many process systems may have been omitted. I have tried to illustrate the multitude of opportunities and the fact that the availability of an economical process for regeneration is not necessarily enough. Instead of leaving waste treatment problems completely in the hands of the environmental engineer, the processing engineer first should reevaluate his processing methods from a pollution abatement and treatment cost standpoint.

**DISCUSSION**

**GAYLORD-GAF Corp:** Please discuss the removal and recovery or disposal of mixed metals from streams containing substantial quantities of organic materials.

**LANCY:** The economical recovery of metals from mixed streams is not too promising. We believe that one of the most important steps when metal recovery is contemplated is to go as close to the process from which the metal is discharged and before any mixing has occurred. One of the reasons for recommending regeneration, if possible, is that recovery is possible before the waste is discharged, and the process solution can be maintained in a closed loop, avoiding even unnecessary dilution.