‘Consume Saving of Water and Energy Through Minimization’

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Abstract

Surface processes consume a great amount of water and energy. Process water should be previously treated in order to minimize alkaline salts in it, decrease conductivity and filtered with active carbon. The water for the process should be previously analyzed.

Water is consumed by contamination of the bath, due to dragging and evaporation. Therefore, partial processes should be minimized. Also, eductors should be installed for good homogenization mixture in the water. Metallic cations and sales should be eliminated by membranes, ionic interchanging columns, active carbon or diatomaceous earth.

Minimization for partial processes and both water and energy recovery should be done at the same time by applying the best available techniques (BAT). It is important for saving on process and products.

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Economic Issues for Recycling vs. Contract Disposal

Currently, our best figures for off-site disposal have been computed for electroless nickel plating waste. Contactors typically quote about euros 110/ton to remove and dispose of liquid nickel waste. Thus, a 3000 L batch of waste costs about euros 540 for off-site disposal.

Previous wokl from our research team has resulted in the establishment of a prototype nickel recovery system that has been placed in the plant at Sant Andres dela Barca, Barcelona, Spain. This recovery system is a flow-through split-cell design using expanded steel mesh cathodes and a propietary anode. The economics of nickel recovery are based on a typical nickel concentration of 11 g/L in a spent bath. electrolysis of the material at 7.5 volts and 180 amps for 200 hr (350 KWH) permits recovery of about 32 kg aprox. of nickel metal and a reduction in nickel concentration in the bath to less than 7-10 ppm.

The cost of this process is euros 25 for electricity at euros 0.91/KWH, euros 12/bath for ammonium hydroxide to control pH, and about euros 30 for the cathodes, which cannot by recycled. Net cost is approximately euros 9082 for a 3000 L spent nickel bath.

The value of the recovered nickel varies with the world nickel market, but will bring about $52.00/kg (in the international metal market) from a nickel refiner in one-ton lots, assuming a market price of $65/kg for refined nickel. This brings euros 315 to the revenue side of the recycling effort, or a net gain of euros 150 for the effort.

An additional cost not accounted for in the process of nickel recovery is labor, which should be nominal (less than two hours total for a cycle) since the only active participation of the staff in the recycle process is periodic and rapid monitoring and correction of pH. The cost of amortization and maintenance of recycling equipment has also not been calculated, and must be configured into the recovery cost.

The Current Nickel Recovery Process Does Not Eliminate Off-site Disposal

Unfortunately, the residual solution from the nickel bath cannot be sent to the sanitary sewer system because of the high level of phosphorus in the system, primarily in the form of hypophosphorous and hypophosphorous acid. Hence the disposal costs for material to be hauled away by a waste processor is not reduced.

The summary of the economic evaluation of the two approaches as currently used are shown in **Table 1**. It is apparent that weight the current approach to Ni capture, little savings are notable. The place where the largest difference seems possible is in reduction of the contractor costs fro removing the waste from the production site for disposal. Logically, this is the point at which research can return the greatest benefits.

Precipitation of phosphate in the form of Ca complexes is a well-established and accepted form of disposal of phosphorous acid to phosphoric acid would permit near quantitative precipitation using lime. But this process has not been perfected, despite the fact that it impact almost all electroless plating processes worldwide.

The difficulty in conversion of phosphite to phosphate and the high phosphorous content of residual nickel baths are twin problems common to the electroless plating industry, and is a research issue worthy of closer study.

Estimated Cost in € per 3000 L Batch (not including labor and capital cost)		
Item	**Electrolysis and off-site disposal**	**Off-site disposal only**
Electricity	32	0
Reagents	18	0
Cathodes	40	0
Contractor*	1500	1500
Nickel Sale	-140	0
Net Cost	490	590

Tab1e. 1 Summary of Ni disposal costs.

*Typical charges for contrator to remove 3000 L of waste from production site for disposal.

In the next year, our research team intends to mores closely evaluate processes for converting the phosphorus load to phosphate species which can be landfilled, permitting normal sanitary sewer disposal of the nickel-depleted and phosphorus-depleted baths.

Literature procedures for oxidation of phosphite will be tried under a variety of conditions to study the limitations of the systems and effects of modifications of the processes on conversion to phosphate. The process will be followed by P NMR.

Until the problem disposal of phosphorus from electroless nickel baths is solved, it will not be difficult to justify nickel capture on economic grounds alone.

Zinc Recovery

The cleanup of zinc water streams has inherently fewer problems that does de cleanup of electroless nickel. First, zinc is easily capture by en electrolytic process in reasonable quality, and this is in fact the primary method of isolation form ore, and of course the basis of plating. The large hydrogen overvoltage permits low pH capture at high efficiencies. Thus, in our laboratory, we have been experimenting with developing model conditions for plating out zinc at about 65% electrochemical efficiency. These model conditions were used to determine useful anode/cathode combinations.

Second, the wastewater from the zinc recovery baths can be sent to sanitary sewer once target levels of zinc are reached. Secondary pollutants such as phosphate are not a major issue.

Current methods for zinc disposal call for precipitation of the metal as the hydroxide dewatering and sending to and approved landfill. We have not yet completed the analysis of the basic cost of this process, but for each plant, this will entail the following: cost of gas or electricity in the drying, cost of filters, and cost of hauling and landfilling the zinc-containing residue. Also, the capital investment needs to be considered. Our team will be evaluating these costs in the near future.

It is unlikely that zinc recovered from plating baths will bear a sufficient price to justify re-refining. Current market pride for plating quality zinc is about $3.10/kg (international metal market). Thus, total recycle in the plant becomes an extremely attractive proposition.

Our initial venture into zinc recovery began with the idea that is may be feasible to return zinc to the plating bath as the sulphate salt. While this is feasible, it offers no real economic advantage to the overall process. We had considered two options: capture on a matrix that would allow either melting of the zinc from the cathode or electrolytic dissolution in sulphuric acid. For this purpose, we considered both aluminium and tugsten cathodes.

Tungsten had the advantage that is has a very high melting temperature. While it was suitable for capture of Zn, there would be no particular advantage with this material over use of zinc itself as a cathode. Electrolytic dissolution of the zinc in sulphuric acid was confounded by a tendency of the tungsten to anodize and interfere with release of zinc back into solution.

Aluminium is used commercially as the cathode to trap zinc from ores, and it is an effective cathode in the laboratory setting, but in a plan setting, the may not provide an optimum stable material as a cathode, especially for periods when pH control has not been effectively maintained. Thus, the real possibility of aluminium contamination of plating baths reduced our enthusiasm for the matrix. Although aluminium may not overtly affect zinc plating, its presence in the bath would constitute another variable in the plating process and is disposal.

After considering several options, it became apparent that the simplest and least expensive solution -use of zinc cathodes for capture of zinc metal from the baths- would provide the best source of high-quality zinc for direct recycle into the plating bath. The other options were explored because they offered the opportunity for purification of materials prior to final inclusion in the bath. Although this opportunity is of great academic interest, the suggestion of such intermediate steps was met with no enthusiasm from those who need a workable process in-house.

We found that we could effectively use anodic materials other that lead. Lead works well because it tends to rapidly anodize and not dissolve into the medium. However, situations can be envisioned where improper setup or maintenance of equipment could introduce lead in into the waste stream. We found that graphite works effectively as an anode. It is not as resilient as other materials, but produces only side-products (some graphite powder if handled roughly) that can be addressed by normal sewage treatment. Tungsten is another inexpensive option, since it rapidly anodize. But graphite become the preferred anode material because of price, availability and environment inertness.

Prototype Zinc Recovery Unit

A four-inch piece of Schedule 35 polyvinyl chloride pipe has been fitted with an inlet containing a valve, an outlet port and 8 cathodes constructed of galvanized screen and wire weaving at 3 mm intervals. The cathodes are placed at about 8 cm intervals. Between each screen pair is one of 6 graphite anodes (ca 9 mm) which penetrates from top to bottom of the pipe. All plumbing and electrical connections are placed at the top to permit optimum leak resistance and out gassing.

These anode and cathode configurations will permit preliminary evaluation of the efficiency of the capture process and provide a basis from which configuration changes can be compared. Eventually, the galvanized mesh will be replaced with pure zinc mesh, and the number and type of graphite anodes will be evaluated to establish an optimum.

The use of this device is in its preliminary testing phase. Our research team will be evaluating its application to drag-out zinc rinse from the Sant Andreu de la Barca, Barcelona, Spain Plant. Result of the efficiency of capture and purity of the capture material will be obtained over the next few months and will be discussed.

We have to bear in mind factors important for the environment and their impact in it, such as the use of some products. It means than minimization has to be applied to reduced contamination of water, air and solid means but also to consider macro price increase for metals (Ni, Cu, Zn).

Therefore, controllable factors affecting operation costs in the electroplating industry include the following:

- Water consumption and wastewater discharge
- Consumption of plating chemicals
- Consumption of chemicals for wastewater treatment
- Disposal of wastewater treatment wastes

The challenge in achieving efficient cost management is to minimize costs associated with these factors without increasing costs elsewhere. For example, reducing water consumption is a cost saving and easy to accomplish. However, it is not a practical cost savings if it results in contaminated plating solutions and poor quality products.

Drag Out Recovery

The first step to meet the challenge is to recover plating solution drag out. This can be accomplished by utilizing a multi-station, stagnant-flow tank as a “pre-rinse”. At least two stations within one tank or two tanks in series are requires. If floor space allows, utilizing additional tanks can increase the efficiency of the drag out recovery. The practical effectiveness of using additional tanks to achieve increased recovery efficiency would need to be evaluated on a case-by-case basis. The purpose of this concept is to establish a counterflow-like system to concentrate the drag out in the first station and use it to replenish solution volume loses in the plating tank. The water volume that would have been added to the plating tank is instead added to the last drag our-station The displaced volume in the last station flows into the previous station until the first station is filled back to its original volume. The transfer of solution can be accomplished via gravity flow, if properly installed, or by using pumps. This process keeps the last station “clean”, because the plating tank is usually much larger in volume that the last station, because the plating tank is usually much larger in volume than the last station. Therefore, a high turnover rate of water in the last station is achieved.

Rinse Water Conservation

Because the drag out recovery system also acts as a pre-rinse, water consumption requirements for rinsing are reduced. However, additional measures are needed to ensure complete rinsing. By utilizing another multi-station tank or multiple tanks in series in the same manner as the drag our recovery method, water consumption requirements can be further reduced and still achieve complete rinsing. The first station would be stagnant, although it is recommended that it be aerated to facilitate through rinsing, if only two stations are used. The last station or tank would be for overflow rinsing, as needed. If additional stations or tanks are utilized, the aeration should occur in the last station or tank before de overflow rinsing. To minimize water consumption as much as possible, water from the first stations or tank can be used for “filling” the last station in de drag our recovery system. The last station in the rinsing process is then overflowed to replace from the first station. As with the drag out recovery system, the transfer can be accomplished by gravity flow or pumping. The last station would also have the capability for overflow discharge to the wastewater treatment system, whenever needed. The amount of water needed for overflow rinsing would be determined on a par-by-part basis and should be only enough to ensure complete rinsing. Ideally, the final station would also be a stagnant rinse tank the majority of the time.

The combination of the drag out recovery system and the multi-station rinsing system conserves plating chemicals significantly reduces water consumption (eliminates water consumption for plating solution replenishing),n and reduces the flow of wastewater, which reduces chemical consumption for its treatment. A reduction in waste generation from wastewater treatment operations is also achieved.

At this point, a method for appreciably reducing the operational cost factors addressed in this paper has been presented. However, additional reductions remain attainable. Further reductions in water consumption and wastewater discharge can be achieved. To obtain these reductions, the concept of zero discharge must be implemented.

Summary

Existing processed for capture of metals from plating waste have been evaluated. Nickel recycling currently provides only modest economic benefit, with most of the benefits of nickel capture and recycling falling into the intangible category or reduction of liability. In order for nickel recycling from planting waste to achieve more significant economic impetus, it will be necessary to address de issue of conversion of phosphorous species to phosphate.

Zinc capture appears to offer the best opportunity for in-house recycling of metals, such that captured zinc can be returned directly to plating baths rather that be sent out for off-site processing or landfilling. Our research team will continue to evaluate its efficiency and potential cost in zinc recycling.

Conclusions

Metal and salts capture should be apply to recover raw materials.

Process waters should no be mixed. It is best to work with closed circuit provided with columns capturing metal cations and anions.

For waste process minimizing and 90 per cent water recovery zero discharge equipment should be used.

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