

Waste Management in Electroplating Industry

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CERTIFICATE

This is to certify that thesis entitled; **"Waste Management in Electroplating Industry"** submitted by Mr. **Anuj Mathur** in partial fulfilment of the requirements for the award of **Masters in Technology Degree in Environmental Science & Technology** at **Thapar University, Patiala (Deemed University)** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.



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Declaration

I, the undersigned hereby declare that the research work presented in the M.Tech project entitled “Waste Management in Electroplating Industry” has been carried out under the guidance of Dr. Nirmala Saraswat, fellow, TERI, New Delhi. Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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Abstract

Waste Management in Electroplating

Definition: Electroplating is one of the varieties of several techniques of metal finishing. It is a technique of deposition of a fine layer of one metal on another through electrolytic process to impart various properties and attributes, such as corrosion protection, enhanced surface hardness, lustre, color, aesthetics, value addition etc.

Electroplating process has applications in large scale manufacturing plants (e.g. automobile, cycle, engineering and numerous other industries) as well as job-work by small and tiny units.

Though this process has a long history, but it gained momentum after independence. In 1976, the first semi-automatic plant was set up in Mumbai. Currently there are more than 600 automatic plants in the county. It is estimated that electroplating is now worth Rs 1000 crores and this sector employs 1, 30,000 approximately people in the industry in 12000 organized sectors. However, hardly any data is available for unorganized sectors and it is difficult to find the distribution of production in unorganized.

Rationale of study

On one hand, the process has number of applications but, simultaneously it has been included among 17 major polluting industries in India by Central Pollution and Control Board, government of India. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes in environment. It was found that a large amount of metals and chemicals is disposed into main stream without treatment as they have no effective measures for treatment or recovery of metals in unorganized sectors.

At the same time it is to be kept in mind that majority of units are in tiny and small scale, which are not able to upgrade the technology immediately to achieve cleaner production. Thus, it is not possible to protect the environment in a significant manner, unless cleaner production is achieved. Consequently, there is a need to adopt a balanced and practical approach so that goal is achieved over a period of time.

In view of its immense relevance, there is a need to plan a strategy that should focus on waste minimization techniques and treatment to control pollution. This is the topic of my thesis entitled “**Waste management in electroplating industry**”.

Objectives

For the thesis we will have the following objectives:

- (A) Collect detailed information on material used in electroplating (like nickel, chromium, silver etc):
 - 1) Different solvents used for surface preparation and pre-treatment
 - 2) Quantification of water used in pre-treatment and post treatment.
 - 3) Quantification of Chemicals in Plating
 - 4) Types of techniques in Chemical Recovery
 - 5) Quantification of sludge production
- (B) Waste minimization techniques
- (C) Recoveries of chemicals from waste rinse water, so that it metals and chemicals can be re-used.

Study Area

My research work is based on the secondary data collected in the survey done in organized sectors of Electroplating Industries in Moradabad, located on banks of river Ramganga, Uttar Pradesh, India. Most of the units operate illegally from the inner city residential areas.

Questionnaires

Data collection was quantitative in nature. Information on classification of industries was collected. The questionnaire was divided in 6 sections:

- a) General information
- b) Information on pre-treatment
- c) Information on plating
- d) Information on post-treatment
- e) Information on chemical recovery
- f) Waste information.

CHAPTER – 1

Introduction

1.1 Introduction

Electroplating is one of the several techniques of metal finishing. It is a technique of deposition of a fine layer of one metal on another through electrolytic process to impart various properties and attributes, such as corrosion-protection, enhanced surface hardness, lustre, colour. They also add to the aesthetic value of object.

Electroplating process has applications in:

- a) Large scale manufacturing plants (e.g. automobile, cycle, engineering and numerous other industries)
- b) Job-work by small and tiny units.

They are spread across the entire country with significant concentration in several states like Punjab, Haryana, Maharashtra, Karnataka, Andhra Pradesh, Tamil Nadu, West Bengal and in some parts of Uttar Pradesh (UP).

1.2 Rationale

The main concern in Electroplating Industry is to control toxic material discharged by it that is why it has been included among 17 major polluting industries in India by Central Pollution Control Board, Government of India. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes in environment.

In order to control pollutants various techniques of treatment of waste are applied. Since, these techniques are very common in practices and are usually followed. These techniques for treatment as well as electroplating process require a large quantity of water, chemicals and equipments which again add the cost of process. Therefore, from economic point of view, there is a requirement to manage waste in a cost-effective

manner. This encompasses two procedures: firstly, minimization of waste and secondly, chemical recovery from wastewater. Thus, in view of above facts, the topic of the project is “Waste Management in Electroplating Industry” is justified.

1.3 Organization of Thesis

Thesis is organized into seven chapters. The main contents of the chapter are described below:

Chapter 1: Introduction:

The chapter is introductory. It discusses the theory of Electroplating and the rationale of thesis.

Chapter 2: Brief History and Present Scenario:

It discusses about the history of electroplating Industry in India and its expansion from place of origin to different parts of country. It also indicate about the annual growth over several decades

Chapter 3: Basic components of electroplating:

The Chapter-3 includes basic principle of electroplating based on Faraday’s law of Electrolysis and an empirical derivation of calculating weight deposited on object and also estimation of loss of electroplating material (anode) produced in an electroplating process. This was established by the help of case study done at Moradabad. It also discusses the optimal conditions required for efficient electroplating process.

Chapter 4: Steps in electroplating and Environmental concerns:

It deals with the different steps that are followed in electroplating process. It gives the detailed information about the process like surface preparation, pre-treatment, plating and post-treatment. It also describes about the different chemicals used and their environmental concerns.

Chapter 5: Waste Minimization Techniques:

This chapter deals with the techniques for minimization of waste generation, by reducing the quantity of water and resources used and recycling of the electrolyte in plating bath.

Chapter 6: Chemical Recovery:

This chapter analyses the recovery of chemicals and metals from the wastewater and electrolytes. It also presents the specific techniques used for specified plating. It also describes the beneficial effects of chemical recovery over the traditional method.

Chapter 7: Summary and Conclusion:

This chapter presents summary and conclusion of project work. Limitation of the work and scope for further research is also discussed in this chapter.

CHAPTER - 2

Literature Review

2.1 Brief History & Present Scenario

Electroplating has a long history in India. Like many other industrial activities, it gained momentum after independence. Modern techniques in electroplating started in early sixties in India, but the first semi automatic plant was set up in 1976 in Mumbai. Since then, the industry has grown steadily without facing any recession. Currently there are more than 600 automatic plants in the country (Comprehensive Industry Document on Electroplating Industry (COINDS)), 2007)

Although official figures are not available, estimates indicate that in 1970, electroplating industry was of Rs. 100 million. During the period 1970-85, the government policy on the restriction import in force led to high growth of this industry (International Metalworkers Federation, 2002).

The growth of the industries is shown in figure 2.1. Though the curve of the growth rises steadily from 1980-2002 but a jump was observed in decade 2002-2012. It is estimated that electroplating industry may now worth Rs. 2000 crores (Rs. 20,000 million) in year 2012.

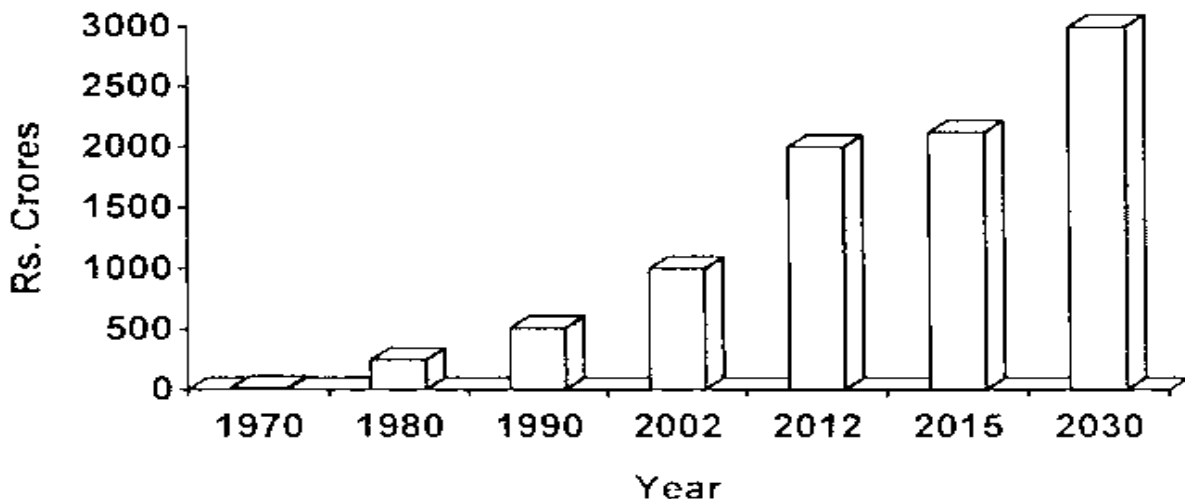


Figure 2.1 Increasing trend and predictions based on growth rate of electroplating Industry in India

(Source: Comprehensive Industry Document on Electroplating Industry (COINDS))

2.2 Consumption of chemicals in electroplating process

Since, the report mentions (Comprehensive Industry Document on Electroplating Industry, COINDS) about the organized units but hardly any data is available for unorganized units. Thus, it is difficult to find out the distribution of production between the organized and small-scale / tiny / unorganized sector. The official figure quoted in the report is that about 1, 30,000 people are employed in approximately 12,000 organized units. However, judging on the basis of the consumption of chemicals and additives, it is estimated that about 18,000 tons are consumed by organized sector, while tiny and unorganized sector consumes about 10,000 tons.

(Source: Comprehensive industrial document, CPCB).

2.3 Review of waste minimization techniques

Though this industry is useful from economic point of view but this industry produces hazardous electroplating waste and is one of the major contributors to heavy metal pollution in surface waters [Ajmal *et al.*, (1993) and Golomb (1972)]. So there is a need to control pollutants present in the waste produced by the process of electroplating.

Over a few decades, a variety of methodologies and technologies for waste minimization have been developed in this industry.

Huang *et al.*, (1991) developed a software MIN-CYANIDE, that contained various solutions and algorithm for waste minimization of cyanide levels produced in electroplating plants. This software also provided Waste Minimization opportunities based on the inputs and also recommended high prioritized measures for source reduction (chemicals). However, the software was restricted to cyanide-containing waste streams only, and was incapable of providing any decision for the support for the minimization of many other chemicals, metal and non-metal containing waste streams.

Other scientists, namely, Y.L. Huang and K.Q. Luo (1997) made an intelligent decision making approach (software called WMEP- advisor) for waste minimization decision support system. But, the program was based on fuzzy linguistic concepts of LOW, MEDIUM and HIGH etc which were related to inputs of electroplating process. So, it

was not able to quantify precisely the LOW, MEDIUM and HIGH inputs, for e.g. EXCESSIVE drag out, HIGH temperature etc.

The common flaw in the above techniques was that none of them have been classified and compared in terms of cost. With the advancement of technology, efforts began for the recovery of chemicals. Several techniques were developed for recovery of chemicals and metals which are listed below.

2.4 Chemical Recovery Techniques

2.4.1 Reverse osmosis (RO)

Sato *et al.*, (1977) developed a metal plating waste water reclamation system which consisted of reuse of waste water from pre-treatment and post-treatment process with the help of RO plant. The waste water discharged from the electro-plating equipment, contained acidic chromium and alkaline cyanides. However, this study proved to be unsuccessful because of the fluctuation in the quality of inflowing waste water, which made the treatment difficult.

Kremen *et al.*, (1977) reported a RO scheme for metal finishing wastewater containing Cu^{2+} , Zn^{2+} , Cr^{3+} and Cr^{6+} , where, 95% of water recovery was found that could be reused in process.

Koga and Ushikoshi (1977) used a RO system to recover valuable paints in electro coating for the surface treatment of aluminum products. It was shown that the plating solution could be reused after RO treatment as rinse water with recoveries of up to 99%. Also, it was estimated that the paints recovery process could result in substantial savings in operating costs.

Kamizawa *et al.*, (1978) studied the treatment of gold plating rinse by RO. They found that the rejection of gold declined from 92% to 82% because of the multi-ion effect.

But, the RO technique was very costly because of the expensive membrane replacement periodically. There was a need to initiate less expensive technique for chemical recovery.

2.4.2. Adsorption Technique for Chemical Recovery

Srinivasan *et al.*, (1988) used Rice husk as an adsorbent for hexavalent Chromium.

Alaets *et al.*, (1989) used carboneous material obtained from Coconut shell to study the adsorption of hexavalent chromium.

Pollard *et al.*, (1992) suggested biomass as an adsorbent over use of activated carbon for adsorption, as activated carbon has high cost of recycling which is a drawback for developing countries.

Sharma and Forster (1993) discovered the sphagnum moss peat to be an effective adsorbent for hexavalent Chromium. But, the recovery of Chromium was only 50%.

Gupta *et al.*, (2009), Sawalha *et al.*, (2009), Wang *et al.*, (2009), Aydin *et al.*, (2008), McKay (1995), Bailey *et al.*, (1999) worked on agricultural residues as low-cost adsorbents for heavy metals in wastewater. They received great attention by developing countries.

Srivastava *et al.*, used waste slurry from fertilizer plants as an adsorbent for heavy metals from electroplating industry.

Salim *et al.*, (2008) suggested that biomass can be used as adsorbent of chemicals used in electroplating industries, Horsfall *et al.*, (2003), Aksu (2001), Wase and Forster (1997), Sandau *et al.*, (1996), Kapoor and Viraraghavan (1995), Holan and Volesky (1995). Coconut fiber was used by Sousa *et al.*, (2008) for adsorption of metals.

Kapoor and Viraraghavan (1998), suggested that acid-treated sugar cane bagasse was more efficient in removal of metal ions than biomass and performed even better than zeolite by re established by Han *et al.*, (2006).

There is a growing interest in using cheap agricultural by-products, such as residues of sugar cane [Amarasinghe and Williams, (2007)].

Column operations having sugarcane residue or bagasse as an adsorbent was developed by Keukeleire and Nascimento (2010) demonstrated recovery of Cu^{2+} , Ni^{2+} and Zn^{2+} from wastewater (in the absence of cyanide) in an electroplating factory were 95.5%, 96.3.0%, and 97.1%, respectively.

However, Huang and Wu (1977) established that adsorption of hexavalent chromium using activated carbon was found that optimum absorption was achieved when pH was maintained at 6.

A comparison between biomass and Activated carbon was done by Monser and Adhoum (2002) and established that use of activated carbon was superior of using sugarcane and bio-mass. But, in developing countries low cost of bio mass can be a crucial factor.

Going retrospectively, Shukla and Sakhardane (1991) made use of sawdust with several reactive dyes for adsorption of Copper (Cu), Lead (Pb), Mercury (Hg) and Iron (Fe).

In highly acidic conditions (pH=2), such as use of chromic acid with sulphuric acid(low pH) Ajmal *et al.*,(1993) reported phosphate treated sawdust showed remarkable adsorption behavior in such conditions. Thus, cost of neutralization can be prevented.

2.4.3 Ion exchange technique for electroplating

Fries and Chew (1993) suggested that Ion exchange appears to be a promising technique for the treatment of streams in electroplating process industries.

Kimbrough *et al.*, (1991) and Stoecker (1999) suggested that separation of heavy metal is based on health concerns (discussed in detail in following chapter-4), since some heavy metals are potentially carcinogenic when inhaled and also due to their commercial value.

Sawdust is a widely available in abundance. It has been reported to exhibit Ion-exchange and complexation capacities towards heavy metals [Begum (1992), Aval and Motedayan, (1991)].

Chmielewski *et al.*,, (1997) used a method for recovering Cr, Cu from electroplating wastewater using a combined process involving electrochemical oxidation and ion exchange.

Carmen *et al.*, (1999) successfully performed recovery of gold using a weak and a strong base ion exchanger.

CHAPTER - 3

Basic components of Electroplating Process

3.1 Components of electroplating process

There are three basic components of electroplating process described as follows:

3.1.1 Electrolyte - A plating bath filled with water and chemicals containing a small amount of acid or alkali added to improve its conductivity. The baths used for plating are called either acid bath or alkaline bath depending upon the chemical used in the bath.

3.1.2 Anode (positive electrode) – Usually this is made of plating metal (Cu, Ni) to be plated on the object. Anode gets consumed as the process of electroplating continues and thus needs to be replenished.

In some cases, this anode could be inert electrode (chromium) and electrolyte contains the material to be plated on the item. In this situation, the electrolyte needs to be replenished.

3.1.3 Cathode (negative electrode) – It is the item/object to be plated. In the case, when the object is hung inside the plating bath, then the process is known Rack, otherwise, when object is placed in a barrel, it is called Barrel plating. Barrel plating has an advantage over rack plating that the material gets deposited evenly on the object due to slow rotation of barrel.

In order to make the plating bath more robust and durable its inner layer is lined with acid or alkali resistant membrane. In order to prevent it from electrical shock it is insulated from polyvinyl chloride (PVC) sheet from outside. Figure 2, shows the basic components of plating.

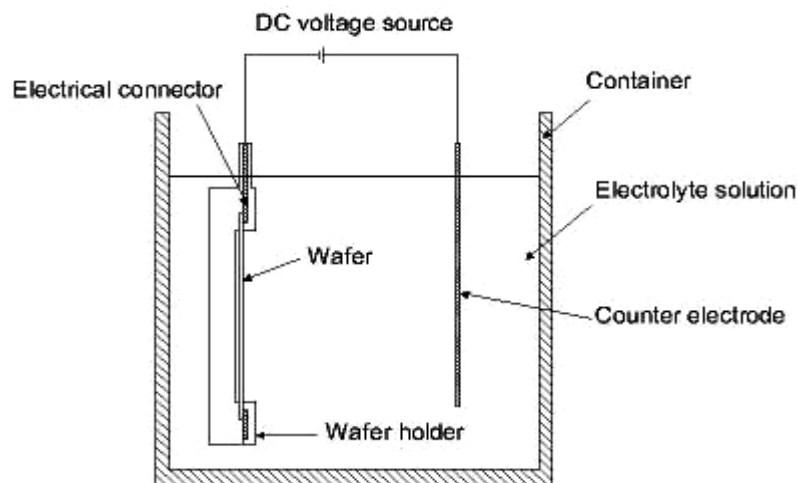


Figure 3.1 showing basic components of electroplating

3.2 Basic principle of Electroplating Process

The anode and cathode in the electroplating cell are both connected to an external supply of direct current - a battery or, a rectifier (if using Alternating Current). The anode is connected to the positive terminal of the supply, and the cathode (article to be plated) is connected to the negative terminal. The process of electrolysis can be explained on the basis of ionization theory. According to this theory, when the direct current is passed the electrolyte dissociates to produce positively and negatively charged ions. The positively charged (cations) ions move towards the cathode whereas negatively charged (anions) ions move towards anode. On reaching their respective electrodes, ions lose their charges and become neutral particles. The cations accept electrons from the cathode to become neutral that gets deposited in the form of metal on cathode, whereas anions gives electrons to anode to become neutral and thus forming electrolyte.

The item to be coated is immersed in the bath solution as the cathode and the coating substance (the anode). However, if an inert electrode is used, the coating substance would be the metal salts in liquid form added to the solution. The metal salts subsequently dissociate into anions and cations, which then deposit onto the items to be plated.

3.3 Quantitative aspects of Electrolysis

The relationship between the amounts of substances liberated at the electrodes during electroplating was explained by Michael Faraday (1833) in the form of two laws:

3.3.1 Faraday's First Law

It states that amount of chemical reaction enhance the mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte.

Thus, if W gram of a substance is deposited in passing Q coulombs of electricity, then

$$W \propto Q$$

$$\text{Or, } W = EQ \text{ ----- (1)}$$

Where, **E is constant of proportionality** called as electrochemical equivalent of metal to be deposited.

If current of **I amperes is passed for t seconds** then equation (1) becomes:

$$W = E \times I \times t \text{ ----- (2)}$$

Electrochemical equivalent can be estimated by measuring mass of the substance deposited on electrode when a current of 1 ampere is passed for 1 second.

3.3.2 Practical consideration in Electroplating

The above formula (2) applies to a reaction which works at 100% efficiency.

But, this is does not happen in practical situation. Therefore, the current efficiency k needs to be introduced.

Thus, the equation becomes,

$$W = \frac{E \times I \times t \times k}{100} \text{ ----- (3)}$$

Now, introducing current density as I_d in ampere/decimetre² (amp/dm²) and converting time into minutes.

$$\text{Then, } W = \frac{E \times I_d \times A \times t \times k}{6000} \text{ grams (g)} \text{----- (4)}$$

Here, A = area in dm^2

The above derived expression obtained for calculating the mass deposited on anode can be verified by the means of a case study as follows.

3.3.3 Empirical Approach to Calculate Waste of Anode in Copper Plating

A case study from plating in Moradabad is considered. Say unit A, is performing copper plating operations. The plater is using Acid copper as electrolyte which has constituents as copper sulphate and sulphuric acid.

Calculating the weight of copper deposited on the cathode using the following values.

Electrochemical equivalent for copper (E) = 1.186

Current density (I) = 1.076 amp/ dm^2

Time (t) = 60 minutes

Area (A) = 1 m^2 = 100 dm^2

Efficiency (k) = 95

Mass deposited (W) is given as:

$$W = \frac{1.186 \times 1.076 \times 100 \times 60 \times 95}{6000}$$

$$W = 0.1213 \text{ kg/m}^2 \text{----- (5)}$$

Now, the plating unit A is electroplating 40 objects per day

Plating area per day = 7.35 m^2

Thus, the unit A is electroplating 2205 m^2 per year (300 working days).

Thus, anode required by unit = 2205 x 0.1213 = 267.46 kg per year

On contrary, the copper as anode consumption per month is 30 kg. Hence, in reality 300 kg of copper as anode is utilized per year (assuming 300 working days or 25 working days in a month)

Electroplating Conversion efficiency = $(267.46 \times 100)/300$

Thus, the actual conversion is 89.1%. Thus, 10.9% of copper anode is lost.

3.3.4 The Faraday's second law

It electrolysis states that, when the same quantity of electricity is passed through different electrolytes connected in series, the weights of the substances deposited at the cathodes are directly proportional to their equivalent weights.

Numerically, it can be expressed as,

$$\frac{\text{Weight of metal 1 deposited}}{\text{equivalent weight of metal 1}} = \frac{\text{Weight of metal 2 deposited}}{\text{equivalent weight of metal 2}} \quad (6)$$

3.4 Optimal Operating Conditions of Electroplating Process

The efficiency of electroplating depends on many factors, which are discussed below:

3.4.1 Temperature

The electroplating process is often exothermic in nature that leads to increase in temperature of plating bath. Though, high temperature has beneficial effect and gives the material crack-free coating, but, also excessive bath temperature reduces the rate of electroplating process and thus, results in formation of soft dull deposit. There is a need to keep the temperature suitable according to material to be plated, that is neither too high nor too less for efficient plating.

3.4.2 Cathode current density

Optimal current density is directly proportional to the bath temperature. Higher is a temperature more the current density is required. Very low current density decreases effectiveness of the plating process. Too high current density may cause **burning**.

3.4.3 Anodes

The ratio of surface area of anode to cathode varies between 1-2. Properly operating anodes are coated with dark brown lead peroxide. If an anode has lighter color (yellow-orange) it should be cleaned.

3.4.4 Power supply

Power supply should be maintained constant during the process. Ripple should not be more than 5%. High ripple exceeding 5% and current interruptions may cause dull or even laminated deposit.

3.4.5 Agitation

Agitation helps to maintain the temperature of bath, which is a pre-requisite condition for electroplating process. It can be done mechanically or by clean air.

3.4.6 Filtration

Continuous filtration of plating baths with filters or active carbon filters helps for removal of foreign particles and organic contaminations (products of brightener decomposition etc). It helps in sustaining the life of plating bath solutions. This will increase the efficiency of the electroplating process. The filtration pumps should turn over the solution a minimum 1-2 times tank volume per hour.

CHAPTER - 4

Steps for Electroplating process

4.1 Main constituents of Electroplating Process:

Majority of metal finishing operations typically involve four principal work steps or process operations which are listed below:

- 1 Surface preparation
- 2 Pre-treatment
- 3 Electroplating
- 4 Post - treatment

4.2 Surface preparation

Surface preparation though is not a part of electroplating process but is necessary for ensuring strong and uniform adhesion of the coating on the substrate. It includes smoothening of the substrate surface (item to be coated) before the plating operation. Surface preparation includes only physical process and no chemicals are used. The surface preparation namely buffing done by scrapper can be done either manually or mechanically (as shown in table 4.1)

4.3 Pre-treatment

This process aims to prepare and remove the contaminants from the items for plating.

Contaminants includes:-

- a) Oil
- b) Grease
- c) Dirt
- d) Mineral oils (Rust protection oils, Cutting fluids, coolants)
- e) Miscellaneous organic soils (paints, fingerprints)
- f) Polishing compounds
- g) Miscellaneous solid particles (dust, abrasive grits, chips)

h) Oxides, scale, smut, rust.

The different activities involved in pre-treatment methods are:

- (i) Acid activation – By mild acids and strong acids
- (ii) By chlorinated hydrocarbons
- (iii) Electro cleaning – cleaning of electrodes by alkali and direct current
- (iv) Ultrasonic cleaning- rarely used technique using high frequency sound waves.

The details of surface preparation and pre-treatment, type of chemicals used with their environmental concerns are summarized in **Table no 4.1**.

Table No 4.1: Different steps for pre treatment and their environmental concerns

Steps	OPERATION	CHEMICALS/ TOOLS	FUNCTIONS	ENVIRONMENTAL CONCERNS*
1) Surface preparation	Buffing	Scraper	Smoothens the surface by scrapping	Powder formed from buffing. If not controlled the dust may enter the respiratory tract and cause breathing problems.
2) Pre-treatment a)	Acid activation	(i) Mild acids like citric, phosphoric acid used for aluminum, zinc castings and other sensitive alloys. (ii) Strong acids- hydrochloric, sulfuric and nitric (steels and stainless steels)	Removes oxides, any deposits/ scales.	Uncontrolled vapour, gases emitted by acids can cause damage to the eyes, nose, throat and lungs.
b)	Cleaning of surface of object	By use of Solvents (chlorinated hydrocarbons such as tetra chloro-ethylene)	Removal of grease, oil, dirt, scales from the surface of the items.	Inhalation of tetra-chloro-ethylene may affect different organs of human like Liver, kidney etc. Long-term inhalation exposure cause reproductive problems, such as spontaneous abortions.
c)	Electrocleaning	Alkali and direct	Removal of impurities on	It causes irritation on skin. Overdose can

I.	Anodic electro cleaning (reverse electro cleaning)	current	surface of anode and cathode, solid particles adhered to the surface and oxides.	cause damage to the exposed part. It can also alter the salinity of soil
II.	Cathodic electro cleaning (direct electro cleaning)			
d)	Ultrasonic cleaning	high frequency (20 – 45 kHz) sound waves	Removing solid particles, dirt and smut.	
3	Rinsing	Water or De-mineralized water	Washing of solvent/alkali/ acid/ chemicals adhered during pre-treatment	Water which contains the residual of chemicals in process of washing is equally harmful as chemicals. This wastewater should be treated before disposal.

(Source: compiled from various documents)

The acids/alkali and solvents used for cleaning prove harmful to environment.

4.4 Electro Plating Process of different metals

The basic principle of electroplating has already been discussed in Chapter-3. In this chapter, chemicals and substances used in electroplating of different metals will be discussed. Selection of the chemicals used by electroplaters should take into account, the technology as well as finishing quality of object. Table 4.2 describes variety of chemicals

used for plating of different metals, and categorization of waste as well as the environmental concerns of the process.

Table No. 4.2: Different types of Plating and their environmental concerns

S.No.	Type of Plating	Chemicals used as electrolyte and additives	Applications	Waste generated	Environmental concerns
1	Brass	(i) Sodium cyanide, copper cyanide, zinc cyanide and Sodium carbonate (ii) Alkaline pyrophosphate tartarate and Histidine	1.) Brass plating is used in coating on steel wire cord, used in tyres as it provides good adhesion to steel and rubber. 2.) Gold-colored brass often is used as a decorative. 3.) It is also used in parts in engineering finishes.	Cyanide vapours	Cyanide being highly poisonous may affect the biota. Also, cyanide vapours emitted may causes headache, nausea, dizziness and difficulty in breathing

2	Bronze	Copper cyanide, sodium cyanide, Na_2SnO_2 and sodium hydroxide	1.) Yellow bronze may also be used as for finishing, where it is a suitable imitation for gold used in bathroom fittings, furniture hardware etc	Cyanide vapours	High concentrations may cause unconsciousness, abnormal heart rhythm, coma and even may lead to death
				Volatile organic Carbons (VOC) emission	No detrimental effect on health
3	Cadmium	Cadmium Cyanide, Sodium Cyanide, Sodium Carbonate and sodium Hydroxide	1.) Cadmium electroplating is widely used in aircraft industry due to the excellent corrosion resistant 2.) It can be dyed to many colors, has good lubricity and solder ability, and works well either as a final finish or as a paint base.	Cadmium vapours	Irritation of respiratory system, sore and dry throat, chest pain and breathing problems. A long term exposure effect includes kidney damage and is a suspected carcinogen.
				Cyanide vapours and VOC emission	Long term exposure to low levels of cyanide may affect the nervous system

4	Chromium	Chromic acid, sulphuric acid, sodium fluoride	1.) Thin layer of chromium, (below 1 μm thickness) is used on automotive parts (interior and exterior), plumbing fixtures, metal furniture, hand tools, bicycles. 2.) For wear-resistance, they are used in Hydraulic cylinders and rods, industrial rolls, diesel engine cylinders, automotive engine valve stems and piston rings, plastic molds, metal forming tools, cutting tools	Hexavalent chromium vapours,	Hexavalent chromium causes lung cancer in humans. These can cause damage cornea of the eye and can affect nose and throat, with frequent nosebleeds. After many years of exposure, burns in the nostrils are especially slow to heal and may develop into open, oozing sores (ulcers)
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5	Copper	(i) Copper cyanide, sodium cyanide, sodium hydroxide and sodium carbonate	1) The process is used primarily in printed wire board manufacturing and electroforming operations	Cyanide vapours	Cyanide vapours emitted may causes headache, nausea, dizziness and difficulty in breathing.
		1) Copper pyrophosphate, Potassium Pyrophosphate and Ammonium Hydroxide		VOC emission	No detrimental effect
		2) Copper sulphate and Sulphuric acid		Acid mist	It can cause serious damage to the eyes, nose, throat and lungs
		3) Copper Fluoroborate, Fluoroboric Acid, Boric Acid and hydrofluoric (HF) acid		Hydrogen Fluoride (HF) vapours	Chronic exposure of HF can discolour, damage tooth enamel

6	Gold	(i) Potassium gold cyanide, potassium cyanide, potassium hydroxide and Potassium dichromate	1.) Gold plating of silver is used in the manufacture of artificial jewelry.	Potassium cyanide vapours	Highly toxic in nature and can prove to be life threatening
		(ii) Gold potassium cyanide, potassium chloride and Potassium Phosphite	2.) Gold plating is often used in printed circuit boards.		
		(iii) Gold potassium cyanide, potassium chloride and Citric Acids			
7	Nickel	(i) Nickel sulphate, Nickel chloride, Boric acid and Sulphuric acid	1. It is commonly used in coating of many engineering applications that protects the		Nickel compounds can cause skin allergy and cause a chronic skin condition called

		(ii) Nickel Sulphamate, Nickel chloride and Boric acid	material from corrosion. Applications include oil field valves, rotors, drive shafts, paper handling equipment, fuel rails and optical surfaces for diamond turning etc	Nickel sulphate fumes,	"nickel itch" Nickel fumes have been proven to cause nasal and sinus cancers.
			2. It is also used in door knobs, kitchen utensils, bathroom fixtures, electrical/mechanical tools and office equipment.	Acid mist	Hydrogen chloride vapours can discolor the teeth, and both sulfuric and hydrochloric vapours can also cause erosion of the enamel in exposed teeth
			3.) It is also commonly used as a coating in electronics (printed circuit board manufacturing)	Hydrogen fluoride vapours	Hydrogen fluoride vapours cause digestive disorders, including nausea, vomiting, abdominal cramps and diarrhea

		Nickel chloride, hydrochloric acid and Boric acid Nickel flouborate, Nickel chloride and Boric acid Nickel sulphate, ammonium chloride and boric acid			
8	Palladium	Palladium chloride, ammonium chloride, hydrochloric acid	1.) Palladium plating can be used on watches, jewelry and phones due to its bright and shiny appearance, good corrosion resistance and wear resistance. 2.) Palladium nickel plating can be used for electronic parts as it is cheaper than gold.	Ammonia vapour and Acid mist	Vapours and mists released by acid baths can dissolve in the moist tissue of the eyes, nose, throat and lungs, and cause irritation and burns of the tissues

9	Platinum	(i) Hexachloro platinum, Ammonium phosphate, Ammonium hydroxide Hydrogen	1.) Platinum plating is used for catalytic converters (automotive), surgical and medical equipment, and low voltage, low current applications.	Platinum vapours	It causes respiratory allergies. Diseases such as conjunctivitis, dermatitis, asthma, urticaria etc.
		(ii) Dinitrosulphatoplatinate (II) solution and Sulphuric acid	2.) Platinum plating is also used for anodes and for protecting substrates from harsh chemical environments.	Ammonia vapours	Ammonia gas emits vapors that are suffocating and can lead to serious health problems, even death.
10	Rhodium	Rhodium sulphate and Sulphuric acid	1.) Rhodium plating is most commonly found in jewelry like rings, bracelets, necklaces, and other forms of jewelry in order to increase the longevity of the item and improve its quality.	Rhodium vapours	Contact dermatitis (skin related problem) have been reported in workers

			2.) Rhodium plating can be used on circuits and other metal objects to prevent corrosion and reduce the effects of high temperatures.	Acid mist	
11	Silver	(i) Silver potassium cyanide, Copper cyanide and Potassium cyanide (ii) Silver potassium cyanide, Disodium hydrogen phosphate, Phosphoric acid (iii) Silver, Potassium carbonate, Succinamide (iv) Silver iodide, Sodium iodide, Polyvinyl alcohol, Sodium thiosulfate	1.) The most common usage of silver plating is for ornamentation of jewellery, plates, cups, trophies and medals. 2.) The plating helps in reducing friction and to improve paint adhesion. It is good for conductivity and provides a shield against radiation. 4.) Silver finds application in electronics as a replacement for gold. Variable capacitors require silver plating	Cyanide vapours	Potassium cyanide vapours can cause death.

		(v) Silver chloride, Sodium thiosulfate , Potassium metabisulfite			
12	Tin	(i) Sodium Stannate and Caustic Soda (ii) Stannous Sulphate and Sulphuric Acid (iii) Stannous Fluoborate, Tetrafluoroboric Acid and Boric acid, hydrogen fluoride	1.) Tin is a useful metal for the food processing industry since it is non-toxic, ductile and corrosion resistant. 2.) Tin plating is also widely used in the electronics industry because of its ability to protect the base metal from oxidation thus preserving its solderability.	Alkali vapours Acid vapours Hydrogen fluoride vapours	Lower levels of alkali mist can cause dermatitis. Very high vapour exposures can cause pulmonary edema. At relatively low vapour levels, the vapours dissolve before they get deep into the lungs, and the irritation is felt in the upper respiratory system. Hydrofluoric acid in contact with skin destroys tissue. In case, vapours penetrate deep, it can destroy soft tissues and bone, and cause electrolyte imbalance (particularly with calcium).

13	Zinc	(i) Zinc chloride, Potassium chloride, Ammonium chloride, Boric acid	1.) Commonly used on nuts, bolts, metal brackets etc.	Chlorine gas, ammonia vapours	Unpleasant ammonia odour.
		(ii) Zinc cyanide, Sodium cyanide, Sodium hydroxide, Sodium carbonate	2.) It also makes an excellent undercoat for powder coating or paint.	Alkali mist	Persistent vapour exposure can damage the nostrils of the nose.
		(iii) Zinc oxide, Sodium hydroxide			

* Source: compiled from the different documents

4.4.1 Chemicals used in electroplating other than electrolytes and anodes

Apart from the bath chemicals and anode material, other chemical agents are used, which are used for enhancing the electroplating efficiency. Some of them are:

(I) Brightener

In order to achieve bright and lustrous appearance of object to be plated, organic and inorganic chemicals (brighteners) are added to the electrolyte. The different categories of brightener that can be used for specific purpose are as follows:

- a) **Carrier brighteners** like para-toluene sulfonamide and benzene sulphonic acid gives uniform fine Grain structure to the plating.

- b) **Levelers** namely allyl sulfonic acid, formaldehyde chloral hydrate produce are added in combination with carrier brighteners for brilliant deposit.
- c) **Inorganic brighteners** such as cobalt, zinc gives additional luster to the coating of metal.

(II) Wetter

Wetter is used as an anti-pitting agent used in electrolyte with low foaming characteristics which enables it to function equally well in air-agitated or mechanically agitated solutions.

The action of Wetter significantly lowers surface tension of electrolyte, allowing the plating solution to spread uniformly, and provide intimate contact with the surface of metal being plated. As a result, pitting caused by formation of hydrogen bubbles on cathode or other organic contaminations are greatly reduced, or eliminated. E.g. sodium lauryl sulfate

In addition to its effective wetting action, it provides other operational benefits. It does not co-deposit with the metal plate and thus, do not affect deposit characteristics.

4.4.2 Problems faced in using different electrolytes in electroplating

The environmental concerns have been discussed in Table 4.4. Besides, environmental concerns there are some operational problems for different electrolytes used in plating of different metals. Some of these problems have finite solutions while other remains unsolved. These concerns are discussed below:

Problems such as choosing of non-cyanide solution over cyanide solutions on the cost of its dull deposit affects the cost of plated object, needs to be consulted by an expert.

- 1) **Concern:** Alkaline cyanide baths are used from past to till date are used in electroplating. The problem having the alkaline cyanide bath that for obtaining consistent deposit of metals high current densities is required. This affects the cost of the electroplating process.

Action: Hence, platers should use the alkaline cyanide bath for flash deposits of metal (thin layer).

- 2) **Concern:** Traditionally, Cyanide has been used as plating solutions in electroplating Industries. Being, hazardous to the health of humans and thus, has serious environmental concerns (air, water and soil) (refer to Table 4.2).

Action: Hence, Environmental and safety considerations have stimulated the development of cyanide-free plating formulations. Some of these non-cyanide processes have been already implemented in the electroplating industry. A cyanide-zinc solution can be replaced with a non-chelated alkaline zinc solution (Meltzer *et al.*, 1990). Non-cyanide cadmium baths are now available to replace a cyanide cadmium bath (Higgins, 1989)

- 3) **Concern:** The gold colored brass often use as a decorative has the problem of tarnishing (dull brightness) after plating.

Action: The conventional solution to this problem is application of a protective layer of clear transparent powder coat or lacquer to give brighter look.

- 4) **Concern:** Non-cyanide solutions used in electroplating have insufficient colour in the deposits and thus insufficient color. Moreover, the process using non cyanide solution work in narrow operating range (Fujiwara 1993b).

Action: Some additives can be added to non cyanide solutions to maintain the quality of the deposit (For example, additive Histidine is added to Brass pyrophosphate solution for maintaining the conventional quality of brass plating).

- 5) **Concern:** The main disadvantage of copper pyrophosphate is that the preparation of electrolyte is quite expensive and wastewater produced after plating is harder to treat (Braun Intertec 1993).

- 6) **Concern:** Acidic plating bath solutions (For example, Copper plating) have low pH which can attack the object to be plated (Braun Intertec, 1992).

- 7) **Concern:** Fluoroborate bath solutions have fluoride ions which are chemically active and attack the portion of object which is not to be plated.

Action: In order to prevent areas from unwanted plating from fluoride, they should be masked.

- 8) **Concern:** Trivalent chromium (Cr^{3+}) is formed in electroplating process of chromium. Normal level of the trivalent chromium is about 1-2% of the chromic acid concentration. Ions of trivalent chromium continuously re-oxidize to the hexavalent state at the anode. But, higher contents of trivalent chromium (more than 2%) may cause:

- Reduction in Throwing power which causes reduction in plating rate
- Treeing of the deposit.

Action: If the trivalent chromium is too high, re-oxidation operation should be carried out at high anode area/cathode area ratio at specific current density.

4.5 Post Plating Treatment

After performing the plating process, most of the plated objects require post treatment operations. The purpose of Post treatment operations are:

- To enhance the physical appearance of the item.
- To improve the corrosion resistance of the item.
- For enhancing the aesthetic values.

Post plating treatment includes different techniques as following:

1) Sealing

Sealing is conducted in hot water at a temperature about 200°F (93°C). It is done in order to trap the dye which is located in the pores from leaking and prevent absorption of undesired molecules in the pores. The crystals seal the pores opening. Anodize coatings used for application of paints and adhesives.

2) **Dying**

Dying is a process of absorption of organic or inorganic molecules in the pores of object after plating. Dying provides excellent decorative appearance to the plated object. The dye fills the pores and gives color to the coating of plated object.

3) **Conversion Coating**

It is a process of formation of a film of chemical compound on the object surface to prevent corrosion and to limit the growth of salts which may harm due to corrosion. This reaction differs from a conventional coating applied on the substrate surface as it does not change its chemical state. In conversion coating, heavy metals are used as in their high valence state, since they have the ability to prevent corrosion. For eg vanadium, molybdenum, tungsten etc.

Types of conversion coating depending upon the requirement of properties are as follows:

a) Phosphating

Phosphate coating (phosphating) is a conversion coating consisting of an insoluble crystalline metal-phosphate salt formed in a chemical reaction between the substrate metal and a phosphoric acid solution containing ions of metals (zinc, iron or magnesium).

Zinc phosphate coating is applied when high corrosion resistance is required.

Iron phosphate coating is applied when strong adhesion of a subsequent painting is required.

Manganese phosphate coating is applied when wear resistance and anti-galling properties are required. Manganese phosphate also possesses the ability to retain oil, which further improves anti-friction properties and imparts corrosion resistance to the coated parts.

b) Anodizing

Anodizing is an electrochemical process of forming conversion oxide coating by oxidation of an anodically connected metal in an acidic electrolyte solution. Anodizing is mostly used for aluminum. Other commercially anodized metals are tantalum and niobium

c) Black oxide coating

In this process, molten baths are prepared (A mixture of sodium nitrate (NaNO_3) and potassium nitrate (KNO_3) in equal ratio). The bath contains molten oxidizing salts, in which oxygen reacts with iron atoms to form a film of black oxide. It is least expensive of other treatments and gives shiny black appearance which is stable at high temperatures. By this process, there are minor dimensional changes with good lubricating properties which make its application in automotive parts (bearings, springs), cutting tools, gauges etc.

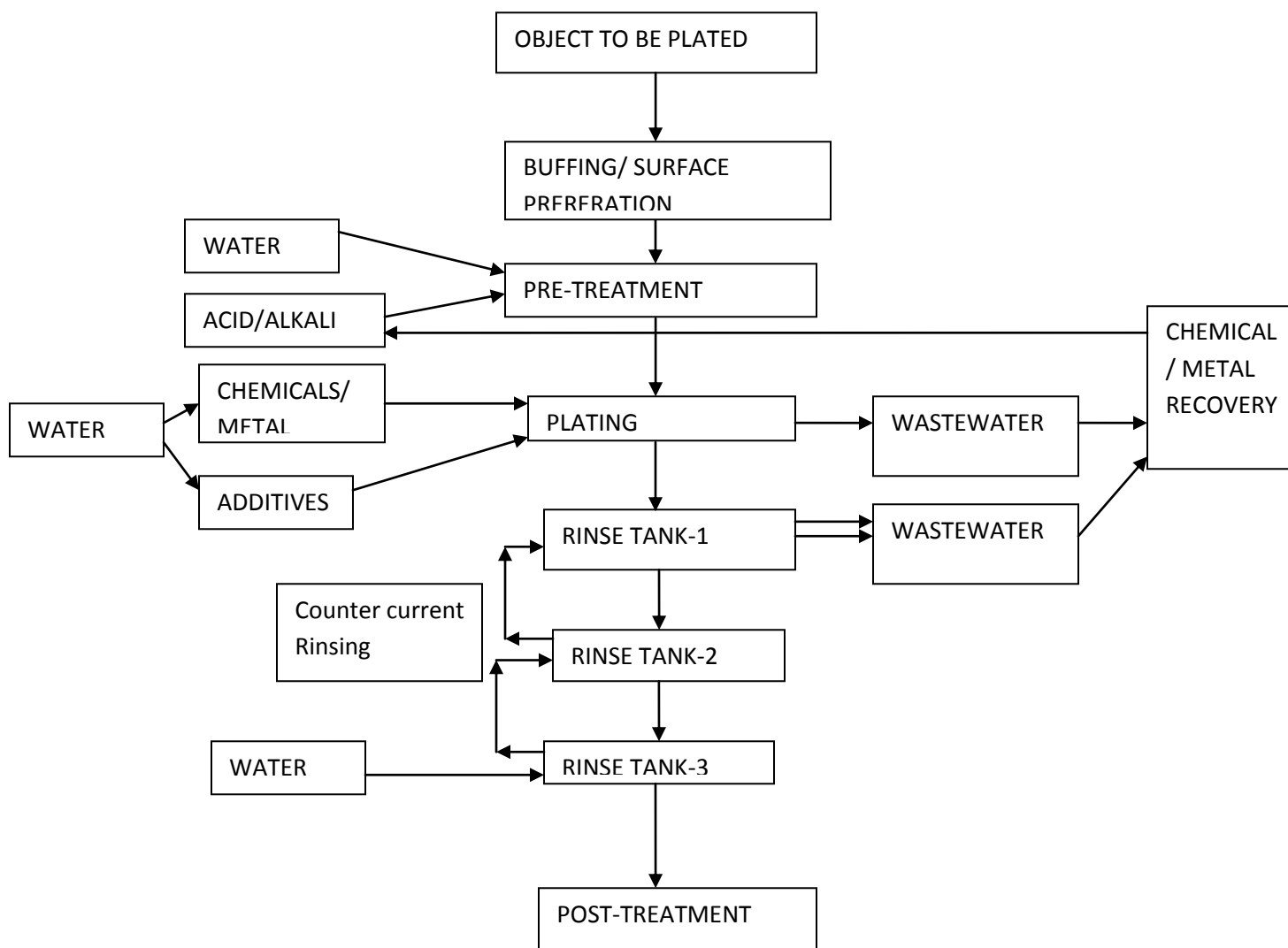


Figure 4.1 TYPICAL FLOW CHART OF ELECTROPLATING PROCESS

CHAPTER - 5

Minimization of waste

5.1 Characterization of Waste generated from Electroplating Industry

Electroplating industry has been generating a huge amount of waste in the forms of wastewater, spent solvent, spent process solutions and sludge (Freeman, 1988). The industry of Electroplating generates wastes in different forms which are solid, liquid and gaseous (Chapter-1) and has been declared under 17 major polluting industries in India by CPCB. Hazardous waste is generated during different steps of the process.

5.1.1 Solid waste generated from the process

Solid waste includes residues such as cleaning powder; buffing compounds generated during the pre-treatment process and spent anodes during the plating process (Chapter-4). In addition to this, when any recovery system (that will be addressed in next chapter) is used the solid waste is generated as spent resins when an Ion exchange method is used for recovery, fouled membrane when RO process is used and clogged medium in case of Electro dialysis.

5.1.2 Liquid wastes

The majority of the waste generated in electroplating process is in liquid form. They pollute the environment more as compared to solids and gases and consequences of uncontrolled affect the health seriously (Table 4.2).

On the basis of severity of the effects Central Pollution Control Board has categorized them as Hazardous waste in schedule 1.

5.1.3 Characterization of Solid and Liquid wastes generated from Electroplating Industry (by CPCB)

According to the Hazardous Waste (Management and Handling) Rules, 2002 and as amended vide S.O. 593 (E) dated 20th May, 2003, the following wastes from Electroplating Industry are identified and listed in Schedule 1 as:

1. Acid Residues
2. Alkali Residues
3. Rinse water from pre-treatment and plating operations.
4. Spent bath containing sulphide, cyanide and toxic metals
5. Sludge from bath containing organic solvents
6. Phosphate Sludge.
7. Etching residues.
8. Plating metal sludge
9. Chemical Sludge from wastewater treatment.

5.1.4 Characterization of Gaseous wastes generated from Electroplating Industry

Gaseous emissions come from the plating bath due to high temperature or excessive agitation. Gaseous emission may include the following wastes:

1. Vapours from Chlorinated solvents during pre-treatment
2. Volatile organic Compounds (VOCs)
3. Acid/ Alkali Mist
4. Vapours of Metals (such as Platinum, Hexavalent Chromium, Rhodium, Cadmium etc)
5. Vapours of chemicals (e.g. Nickel sulfamate fumes, Potassium cyanide fumes etc)
6. Cyanide vapours from plating bath.
7. Hydrogen fluoride and Ammonia vapours.

In view of the above mentioned hazardous waste generated in electroplating process, the need for controlling the waste generated is considered as the most important need of the day. In view of its immense relevance, various techniques to control waste have been developed.

Type					
Solid	Spent anodes, buffing compounds, spent anodes, spent resins and fouled membranes (During chemical recovery), sludge				
Liquid	Rinse water from pre-treatment and plating operations, spent bath containing sulphide, cyanide and toxic metals				

5.2 Waste Minimization in Electroplating Industry

Waste minimization occupies the topmost and most important position in management of waste (John Pichtel, 2005).

The basic approach that can be applied to minimize the waste are:

5.4.3 Minimizing the resource use

This is the very first step to be followed for minimizing the waste. The cost of the process depends heavily on the initial planning required for the purchase of raw material termed as Inventory Planning.

Usually, the raw material is purchased in excess due to lack of planning that results in:

- a) Purchase of excess of raw material remains unused and thus enhances the cost of process.
- b) In case of excess of raw material there is a tendency to overuse the surplus raw material. This will lead to higher generation of waste.

5.4.4 Modifying the process

The use of machines or electronic sensors can improve over the process using the manpower.

5.4.4.1 The use of sensors

Water level sensors are present to indicate level of water in tanks instead of human intervention will definitely improve the efficiency of the process. By modifying the process, the efficiency of process can be increased and waste generation can be minimized.

5.4.4.2 Use of suitable plating baths

The simple way of calculating amount of electrolyte using basic principle of chemistry can help in deciding the size of bath. Thus, smaller size of bath (optimal range) will reduce the waste generation.

5.4.4.3 Using sludge drier in place of using sludge press will minimize the waste stream.

5.4.5 Modifying the product.

Use of product substitution of certain chemicals is a better way to reduce hazardous wastes. For eg. trichloro-ethylene is generated as small waste stream during pre-treatment (Chapter-4). Trichloroethylene is used to clean parts before plating. This can be easily replaced by another solvent that cleans effectively i.e. Isopropyl alcohol. Another example use of non cyanide alternatives over cyanide solutions produces less hazardous waste.

Some of the techniques that can be adopted to minimize waste production in electroplating industry are suggested as follows:

5.3 Minimization of drag-out losses

When plated parts are withdrawn from a plating process unit, they retain some part of the plating bath solution, termed as “drag-out”. The drag out that cause loss of material should be minimized to save both chemicals and water used for rinsing. This process of loss of drag out loss can be minimized in following ways:

- (i) By providing sufficient drainage time so that excess of electrolyte falls in plating tank and can be further reused.
- (ii) Drain board system can be installed between the plating tank and rinse tanks. By this way the excess of the solution dripping from object is collected and recycled to plating tank.
- (iii) Reducing the speed of withdrawal of object from bath tank to drag out tank.
- (iv) The concentrations of process bath can be lowered. As it is evident, less concentrated solution will require less amount of water for rinsing leading to reduction in generation of wastewater.
- (v) Use of surfactants (eg sodium lauryl, discussed in chapter-4) prevents the plating solution to adhere to the object. Thus minimizing amount of drag out.
- (vi) The temperature of plating bath can be increased (within the optimal range). The increased temperature will decrease the viscosity of the plating process solution and hence, less amount of the solution will stick to the object which can be easily removed during rinsing.

5.4 Modified Rinsing techniques

Once the plating operation is over, the plated object is put in a Drag out tank.

Drag out tank is a rinse tank that is filled with pure water for rinsing the plated object. Usually, more than one tank is available for rinsing. 90% of the water used in electroplating industry is consumed in rinsing (estimate given by survey done in Moradabad). We can minimize water use by providing different rinsing techniques.

5.4.1 Counter current rinsing

Countercurrent rinsing consists of series of rinse tanks arranged in which the water flows in the opposite direction of the work flow (dirtiest to cleanest). In order to minimize the use of water required for rinsing, the water of the farthest tank (having least concentration) is transferred to the preceding tank (having higher concentration in comparison to succeeding tank) (figure 5.1). The transfer can be done by mechanical valves, pumps or manually. This technique is termed counter flow (or countercurrent) rinsing because the plated piece and the rinse water move in opposite directions.

The efficiency of counter current rinsing technique increases with the number of counter flow rinse tanks (three-stage, four-stage, etc.) and lower the rinse rate needed for adequate removal of the process solution from object. The technique of counter current rinsing is generally not adopted in unorganized sectors. This was noticed during the survey done at Moradabad where, the platers were having 2-3 tanks for rinsing but were throwing the water of all the tanks. So, this technique can be recommended for conserving water (Chapter-7).

5.4.1. Factors affecting Counter-current rinsing

The efficiency of counter current rinsing technique increases with the number of counter flow rinse tanks (three-stage, four-stage, etc.) and lower the rinse rate needed for

adequate removal of the process solution from object. The rinse rate required for adequate cleaning is governed by following factors:

- (i) The concentration of plating chemicals in the drag-out.
- (ii) The concentration of plating chemicals that can be allowed in the final rinse tank
- (iii) The number of counter flow rinse tanks.

More typically, each added rinse stage reduces rinse water use by 50 percent.

5.4.1.2 Case study of counter current rinsing

Case study was done at Moradabad. Considering, a nickel plating unit B, was utilizing 2 rinse tanks for rinsing and consuming 2250 litres per day.

A typical Watts nickel plating solution contains 210000 mg/l(C_t), and the allowed final rinse concentration(C_r) is 5 mg/l (Existing standards of plating).

Now, estimating the drag out rate of the electroplating process.

Typically, Nickel bath solutions of around 0.1 litre per sq. m. of plated area is lost as drag out to the rinse tanks (COINDS)

Area plated by unit B per day = 7.776 m^2

Hence, the drag out rate for Nickel plating = $7.776 \times 0.1 = 0.7776 \text{ litres/day}$

Now, water requirement for rinsing per liter of drag out by the above equation (6) is
= $0.7776 \times 204.93 = 159.3 \text{ litres/ day}$

Input concentration of object (Nickel electrolyte) = 210000 mg/l

Final concentration of object after rinsing = 5 mg/l

Considering, the input of water as y and the concentration of water = 0 mg/ litre

Concentration of water coming out after rinsing = z mg/ litre

Now, applying mass balance to the system,

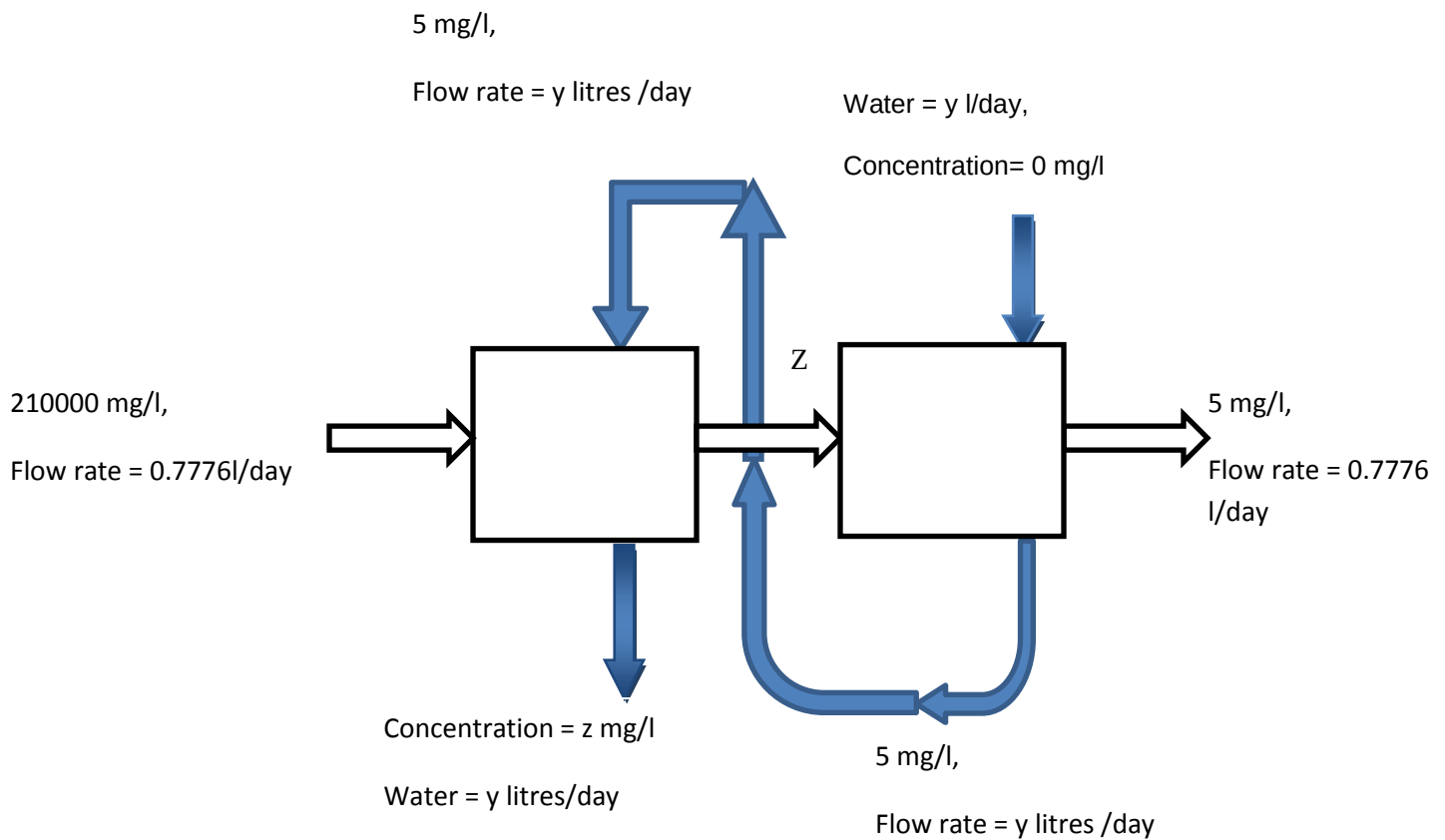


Figure 5.1 Mass balance in two stage counter current system

Forming simultaneous equations from the system,

$$210000 \times 0.7776 + y \times 0 = 5 \times 0.7776 + yz \text{ ----- (i)}$$

$$z \times 0.7776 + y \times 0 = 5y + 5 \times 0.7776 \text{ ----- (ii)}$$

Solving (i) and (ii) simultaneous equations, we obtain the values as:

$$y = 159.2, z = 1025.71$$

Hence, water requirement is 159.2 litres per day

And, the concentration of water after rinsing = 1025.71 mg/l

Hence, for the electroplating unit B, 159.2 litres/ day is required instead of 2250 litres/day.

The mass flow of pollutants exiting the rinse system remains constant.

However, the pollutants are much more concentrated with a two-stage rinse system (1025.71 mg/l) than with a single-tank rinse system (5 mg/l)

5.4.1.3 Estimation of cost for 2 stage Counter current rinsing

The cost of a new two stage counter-current rinse system is about Rs 25,000 (approximately). In addition to this aerator, Poly vinyl chloride (PVC) pipe and connectors and mechanical flow control valves are also required.

The actual cost may be significantly higher depending on the modifications made to the rinse tanks.

Components	Cost (in Rupees)
200 litre tank x 2 (@ Rs 62.5 per litre)	25,000
Aerator	2600
Control valve	500
Pvc pipe and connectors	1000
Total Investment	29,100

Table 5.1 Cost of components of 2 stage counter current rinsing (Source: vendors)

5.4.1.4 Payback period in counter current rinsing

The payback period for installing a counter-current rinse tank will depend on the quantity of water saved and the raw water costs.

In the above case, the two stage system is used to reduce the water flow from 2250 litres/day to 160 litres/day.

The water charges in industries, for the 25-50 kilo litre slab, one kilo litre will cost Rs 50 while consumption of every kilo litre above 50 and below 100 kilo litre will cost Rs 80.

Above 100 kilo litre, the rate is Rs 100 (Uttar Pradesh Jal Board)

Thus, consumption of water per year in case of flow rate 2250 litres/day the cost is Rs 67,500 while after reduction in flow rate (160 litres/day) the cost is reduced to Rs 2400 only.

Steps for calculating payback period

Reduction in cost after using counter current rinsing = $67500 - 2400 = \text{Rs } 65100$

Amount saved per day (assuming 300 working days) = $65100/300 = \text{Rs } 217$

Time taken to recover the cost of 2 stage counter current = $\frac{\text{total cost of equipment}}{\text{Amount saved per day}}$

$$= 29100/217 = 134.10 \text{ days} \simeq 134 \text{ days}$$

$$= 134/25 = 5.3 \text{ months}$$

Thus, the payback period of the whole system is 5.3 months ----- (7)

The savings will be Rs 65,000 per annum ----- (8)

5.4.1.5 Disadvantages of counter current rinsing

Counter flow rinsing systems are not without drawbacks. The negative aspects of counter flow rinsing include:

- (1) Cost of additional rinse tanks
- (2) Loss of valuable production space
- (3) Increase in production time/labor.

5.4.2 Spray Rinsing Technique

Spray rinsing is used to reduce drag-out losses and save rinse water. This includes, rinsing done by spraying over the plating tanks and removes the excess of the electrolyte which drips out in the plating tank itself. In this manner, the electrolyte is replenished. But, the major drawback is that electrolyte gets diluted if spraying is done over the tank. In order to overcome this problem, the process was modified and separate spray rinse tanks (drag out tank) with single or multiple rinses were suggested.

Another design is partitioning of the spray tank into two parts. In the lower part, the dripping of electrolyte takes place and in upper part spray rinsing is done. Thus, it is the combination of both spray and drip rinse tank designs. After plating operation, the object is lowered into the drip portion of the tank. A weir is located at approximately in middle of the tank which maintains the level of solution of dripped electrolyte in the tank. Then, raised above the weir, and sprayed with fresh water (figure 5.2)



Figure 5.2: Circular rinsing tank (This tank is fitted with a circular overflow and a top-spray rinsing)

(Source: surface technology solutions)

Although it is less commonly used, a spray rinse can be used as an alternative for a drag-out tank. This combination rinse can be nearly as effective as a counter flow rinse, and takes up the floor space of one tank.

Spray rinsing is effective for flat-surfaced parts. Depending on the shape of object that has been plated, spray rinsing generally consumes from one-eighth to one-fourth the amount of water that would be used for dip rinsing (Martin Goosey and Rod Kellner, 2009).

5.4.2.1 Spray Rinsing Case Study

In order to compare this technique with view in consumption of water spray rinsing technique is applied to same case study (counter current method)

Components	Cost (in Rupees)
300 litre tank	18,750
Spray (8 nozzles)	10,640
Control valve	500
Pvc pipe and connectors	1000
Pressure reducer	1200
Total Investment	32,090

Table 5.2 Estimation of cost of components used in spray rinsing (Source: vendors)

5.4.2.2 Payback period in spray rinsing technique

In the above case, the spray rinse system is used to reduce the water flow from 2250 litres/day to 282 litres/day ((One-eighth), Martin Goosey and Rod Kellner, 2009).

Thus, consumption of water per year in case of flow rate 2250 litres/day the cost is Rs 67,500 while after reduction in flow rate (282 litres/day) the cost is reduced to Rs 6800 only.

Steps for calculating payback period

Reduction in cost after using spray rinsing = $67500 - 6800 = \text{Rs } 60,700$

Amount saved per day (assuming 300 working days) = $60700/300 = \text{Rs } 202.33$

Time taken to recover the cost of spray rinsing tank = $\frac{\text{total cost of equipment}}{\text{Amount saved per day}}$
 $= 32090/202.33 = 159 \text{ days}$

$$= 159/25 = 6.3 \text{ months}$$

Thus, the payback period is 6.3 months ----- (9)

The cost savings are Rs 60,000 per annum ----- (10)

On comparison of (7), (8), (9) and (10) it was established that that counter current technology saved Rs 65,000 and payback period is 5.3 months, whereas the spray rinsing saved Rs 60,000 and its payback period is 6.3 months. Thus, counter current technique proved to be better from economic point of view.

5.4.2.3 Problems in spray rinsing

- 1) The most important drawback, which prevents spray rinsing use is that, the chemical recovered after spray rinsing has many contaminations such as brighteners, additives, grease etc, that requires to be separated/purified before the chemical recovered is recycled to the plating bath
- 2) It is less effective with recessed and hidden surfaces.
- 3) The design of spray rinses must consider the size and shape of the part. Spray nozzles are available in many sizes and spray patterns, and should be selected appropriately.
- 4) Higher spray velocities may require pumping.

CHAPTER - 6

Chemical Recovery

6.1 Rationale of Chemical recovery

During electroplating process, electrolyte is consumed partly in deposition of metals on cathode and other part is lost in rinsing of the plated object. The major part of electrolyte is lost in drag out, containing metals (Nickel, silver, copper etc). This flows down as waste in the rinsing process. This wastewater containing the metals and chemicals require strict procedures for treatment and disposal.

The plating bath solution needs to be discarded after some rounds of plating because of increase in impurities that reduces the efficiency of plating process and cause deterioration in quality of deposit. This causes waste in monetary terms and has environmental concerns.

6.2 Different techniques of Chemical/Metal Recovery

Recovery of metals and chemicals from the wastewater generated by rinsing plays an important role in reducing the cost of process and reduce the environmental concerns as well. The recovery of metals or chemicals can be done by adopting various methods. These methods are briefly described below with their specific advantages and disadvantages.

6.2 .1 Evaporation method for Chemical recovery

This is the most convenient and traditional form of chemical recovery.

As more and more plates are rinsed, the concentration of chemicals in the rinse tanks increases due to drag out of plated objects. After some rounds of rinsing, the concentration of chemicals in rinse tanks rises to such an extent that it appears to be equivalent to that of plating bath. In order to make water in rinse tank suitable for

recycling process of evaporation is used. The concentrated chemicals can be recycled in plating bath via pump.

6.2.1.1 Fundamental principle underlying Evaporation process

Every chemical solution is made up of at least one or more solvent, and one or more dissolved materials known as solute. Water is the major solvent used and also for various other processes in different processes in the electroplating industry. Most of the chemicals used by the metal finishing industry are water soluble. Most solvents, including water, have high vapour pressures. Most of the metallic salts used for plating is non-volatile (not vaporize easily), even if heated to very high temperatures. The wide difference in vapor pressure (or relative volatility) between water and bath chemicals facilitate separation of bath drag-out from rinse water (For example, Nickel has boiling point of 3500°C while water has 100°C). This becomes the underlying principle for chemical recovery by evaporation.

6.2.1.2 Process of Evaporation using Atmospheric Evaporator

Atmospheric evaporators consist of air stream to strip water as vapour from rinse tank. Evaporation takes place at room temperature. The air pressure exerted by evaporator increases the rate of evaporation at room temperature and this enables the separation of water from chemicals in drag out. They are widely used by industry because of their low cost and simple operating procedure. Atmospheric evaporator units are used as single or in multiples to dewater plating rinse waters to recover bath concentrate. After removing excess of water from the rinse tanks, the chemicals recovered are recycled to plating bath with the help of a pump.

6.2.1.3 Atmospheric Evaporators Case Study

To illustrate the effectiveness of chemical recovery using atmospheric evaporator a case study was taken from a plating unit C operating in Moradabad.

The wastewater coming out after 2 stage counter current rinsing operation has concentration 1025 mg/l and flow rate is 160 l/ day (values are taken from chapter-5).

Estimate of chemicals wasted in drag out losses in a plating unit C performing nickel plating from Moradabad.

Drag out rate (estimated in Chapter-5) = 0.7776 litres/day

The chemical for nickel plating from a Watt's Nickel bath includes following constituents with composition as follows:

Nickel sulphate = 240 g/l

Nickel chloride = 40 g/l

Boric acid = 30 g/l

Proportion of the constituents of the bath = Boric acid: nickel chloride: nickel sulphate
= 30:40:240 = 1:1.33:8

Therefore,

Amount of nickel sulphate in drag out = $(.7776 \times 8) / 10.33 = 0.602$ l/ day

Amount of nickel chloride in drag out = $(.7776 \times 1.33) / 10.33 = 0.097$ l/day

Amount of Boric acid in drag out = $(.7776 \times 1) / 10.33 = 0.075$ l/day

Density of Nickel sulphate = 3.86 kg/l, density of Nickel chloride = 1.92 kg/l, density of boric acid = 1.43 kg/l

So, mass of Nickel sulphate lost in drag out = $3.86 \times 0.602 = 2.32$ kg/ day

Mass of Nickel chloride lost in drag out = $1.92 \times 0.097 = 0.186$ kg/day

Mass of Boric acid lost in drag out = $1.43 \times 0.075 = 0.107$ kg/day

Mass of Nickel sulphate lost in a year = $2.32 \times 300 = 696$ kg/year

Mass of nickel chloride lost in a year = $0.186 \times 300 = 55.8$ kg/ year

Mass of boric acid lost per year = $0.107 \times 300 = 32.1$ kg/ year

Evaporative systems recover valuable resources, conserve waste-treatment chemicals, and minimize the production of metal hydroxide sludge. Unlike chemical treatment, evaporative recovery provides users a return on investment and helps to lower plating cost [Howard (1982)].

Evaporative recovery systems have proven to be reliable, effective and economical in more than 30 years of field experience. Today's systems are compact, economically efficient, and offer microprocessor-based controls. The economic benefits of such evaporator recovery systems include:

- Partial, open-loop recovery of 90 percent of plating solution.
- Savings in treatment chemicals because only 10 percent of the drag out needs waste treatment.

Hence, with atmospheric evaporation the losses of plating chemicals in drag out are reduced to:

Nickel sulphate = 69.6 kg/year

Nickel chloride = 5.58 kg/year

Boric acid = 3.21 kg/year

Chemicals consumption per month (data taken from Moradabad) = 250kg/month,

6.2.1.3.1 Estimation of cost for atmospheric evaporator

Calculating energy cost

The amount of energy required is roughly 1000 British thermal units (BTU) per pound mass of water evaporated, regardless of whether the evaporation is conducted at atmospheric pressure [William (1998)].

$$1000\text{BTU} / 0.45 \text{ kg} = 2222.22 \text{ BTU/kg}$$

Water to be evaporated in one day = 160 kg

So, 160 kg of water will require = $160 \times 2222.22 = 355555.56 \text{ BTU}$

Yearly consumption (300 working days) = $300 \times 355555.56 = 106666666.7 \text{ BTU}$

1 therm = 100000 BTU

Also, 10666666.7 BTU = 1066.66 therm

1 therm = 29.4 Kwh

And, 1066.66 therms in terms of kWh or units = $1066.67 \times 29.4 = 31360$ units

Cost per unit in India = Rs 4.65

So, energy cost of evaporator per year = $4.65 \times 31360 = \text{Rs } 145824$

Components	Cost (in Rupees)
Atmospheric evaporator system	117391*
energy cost /year	145824
Total Investment	278932

Table 6.1 Cost details of atmospheric evaporator

(*Source: vendor's website)

6.2.1.3.2 Calculating the savings

The water will be evaporated from the first tank of 2 stage counter current system having concentration 1025.71 mg/litre and flow rate as 160 litres/day (values taken from Chapter-5)

Cost of nickel sulphate per kg = Rs 178

Cost of nickel chloride per kg = Rs 360

Cost of Boric acid per kg = Rs 70

Savings of nickel sulphate per year = $626.4 \times 178 = \text{Rs } 111500$

Savings of nickel chloride per year = $50.22 \times 360 = \text{Rs } 18080$

Savings of boric acid per year = $28.89 \times 70 = \text{Rs } 2022.3$

Total savings per year = $111500 + 18080 + 2022 = \text{Rs } 131602$

6.2.1.3.3 Payback period using atmospheric evaporator

Amount saved per day from savings (assuming 300 working days = $131602/300$
= Rs 438.6

Payback period for the equipment cost = $117391/438.6 = 267.6$ days ~ 268 days
= 10.7 months (300 working days)

Thus, payback period is 11 months (assuming 300 working days).

The cost of electricity per year = Rs 145824

But, the savings per year are Rs 131602. Thus, this system will not be beneficial from economic point of view for the above plating unit. But, it can be successfully applied to bigger plating units.

6.2.1.4 Disadvantages of Evaporator

- 1) The major drawback of evaporation is that removal of water from wastewater recovers the chemicals which can be recycled but it also contains impurities such as degraded brighteners, sodium and tap-water contaminants which do not get separated. Thus, the impurities present in the chemicals decreases the efficiency of process.
- 2) During this process, the pH value of wastewater stream gets changes to acidic and become unsuitable by causing unwanted chemical reactions such as the production of low solubility products, or the possible decomposition of certain chemicals or release of acidic gases.

6.2.2 Ion-Exchange

Whenever an ion is removed out of an aqueous solution and is replaced by another ionic species, this is what we generally refer to as “ion exchange”. There are synthetic materials available that have been specially designed to enable ion exchange operations at

high performance levels. “Ion exchangers” can be used in processes of environmental protection such as purification, decontamination, recycling or even for the design of new environment-friendly production processes.

6.2.2.1 Principle of Ion exchange process

To each of the monomer units of the polymer, “functional groups” are attached. These functional groups can interact with water soluble species, especially with ions. Ions are either positively (cations) or negatively (anions) charged. Since, the functional groups are also charged; the interaction between ions and functional groups is exhibited by electrostatic forces. Positively charged functional groups (For example, a quarternary amine) interact with anions and negatively charged functional group (For example, a sulfonic -, phosphonic - or carboxylic acid group) will interact with cations.

The binding force between the functional group and the attached ion is relatively loose. The exchange can be reversed by another ion passing across the functional group.

The adsorption of different kinds of cations on ion exchange materials was studied and it was found that different ions do interact differently with the functional groups of ion exchangers.

Some are strongly bound, some are less strongly bound. This results in the fact, that a weakly bound ion can preferably be displaced by a stronger binding ion. This effect is called the principle of “selectivity”. A more selective ion binds more strongly than a less selective ion. The effect of selectivity can be used to remove distinct ions from water and to replace them with other ions.

The ion exchange continues as long as there are enough selective ions available for the resin to exchange and/or until the functional groups are saturated with the selective ions. Thus, the equilibrium is reached when the binding sites on functional group gets saturated. The next step in the procedure will require regeneration of resin.

6.2.2.2 Regeneration of ion exchange resin

Most ion exchangers can be regenerated by acids (excess of H^+ ions), salt-brines (excess of sodium or chloride ions) or by alkali (excess of OH^- ions).

During regeneration the adsorbed ions are removed and replaced by the ions named above. The spent regenerant solution contains the formerly adsorbed pollutants in a concentrated form. The solutions can be re-used in the production process where the wastewater was generated.

The observed regeneration capacity may differ due to several factors such as:

- a) High levels of total dissolved solids (TDS).
- b) Complexing agents.
- c) Incomplete regeneration.

6.2.2.3 Process of Ion exchange

Wastewater having metals is passed through the columns and the exchange occurs. Chelated resins are a special category of weak cation resins that are very useful in certain heavy metal recovery application. Their pH range is lower for many heavy metals and they are selective. The advantage of low pH range is that the metals do not precipitate as oxides or hydroxides while you try to grab them. Precipitated metals are not removed by ion exchange systems, the metals must be dissolved. Selectivity is a very important feature of chelated resins.

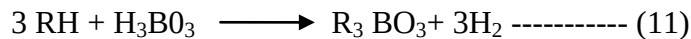
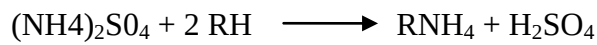
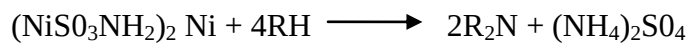
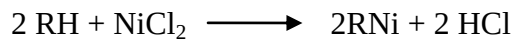
Breakthrough in Ion-exchange

When the resin column becomes saturated with ions and the capacity is almost all used up, leakage increases until the concentration of ions in equals the concentration out. When the leakage starts to increase rapidly, indicating the end of the useful life of the column, breakthrough is said to occur.

The systems are typically operated in cycles consisting of the following steps:

- a) **Service (exhaustion)** - Water solution containing ions is passed through the ion exchange column or bed until the exchange sites are exhausted. The resins may be strong or weak acid/bases resins.

Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO₃H) and salt (R-SO₃Na) form. They can convert a metal salt to the corresponding acid by the reaction. For e.g. for watts nickel plating solution:



- b) **Backwash** - The bed is washed (generally with water) in the reverse direction of the service cycle in order to expand and resettle the resin bed.
- c) **Regeneration** - The exchanger is regenerated by passing a concentrated solution of the ion originally associated with it through the resin bed; usually a strong mineral acid or base.

For example, hydrochloric acid (HCl) regeneration to the above equation (1) would result in a concentrated nickel chloride (NiCl₂) solution

- d) **Rinse** - Excess regenerant is removed from the exchanger; usually by passing water through it.

6.2.2.4 Ion exchange case study

Considering a case study for ion exchange from an electroplating unit D, performing Nickel plating in Moradabad.

After 2 stage counter current rinsing, the wastewater which is generated has concentration 1025 mg/l with flow rate of 160 litres/day (values are taken from chapter-5).

Now, using Ion exchange for this wastewater for the recovery of chemicals with exchange capacity of 30 milliequivalent (meq)/ kg of resin and density of resin is 250 kg/m³.

Determining the mass and volume of resin required to treat 160 litres/ day of wastewater containing 1025 mg/l of concentration.

$$1 \text{ mg/l} = 1/\text{meq wt}$$

$$\text{meq wt} = \text{atomic wt (in mg)} / \text{valency}$$

$$\text{meq wt of Ni}^{2+} = 58693.4 / 2 = 29.34 \text{ meq wt}$$

$$1 \text{ mg/l of Ni}^{2+} = 1/29.34 = 0.034 \text{ meq/l}$$

$$\text{Then, } 1025 \text{ mg/l} = 34.93 \text{ meq/L}$$

$$\text{Hence, required exchange capacity is equal to} = 34.93 \times 160 = 5590 \text{ meq}$$

The required mass of resin as R_{mass} in kg,

$$R_{\text{mass}} = 5590 / 30 = 186.34 \text{ kg of resin}$$

The required volume of resin is given as R_{vol}

$$R_{\text{vol}} = 186.34 / 250 = 0.74 \text{ m}^3$$

$$1 \text{ m}^3 = 35.31 \text{ ft}^3$$

$$0.74 \text{ m}^3 = 26.14 \text{ ft}^3$$

Requirement of regenerant

The ion exchange requires regeneration after every 100 days. Hence, regeneration will be required 3 times a year.

For a Copper or Nickel system, about 1 gallon of 93% sulfuric acid is used per cubic foot of resin. This is diluted to a 15% solution so a total of 11 gallons of regenerant is used per cubic foot (15 lb acid, 85 lb water), [Remco engineering, water systems and tools]

$$\text{Requirement of acid} = 15 \times .45 \times 26.14 = 176.45 \text{ kg}$$

$$\begin{aligned} \text{Requirement of sulfuric acid per year} &= 176.45 \times 3 \text{ (assuming 300 working days)} \\ &= 529 \text{ kg} \end{aligned}$$

$$\text{Cost of regenerant (@Rs 6 per kg)} = \text{Rs } 3174$$

Usually, a little fraction is lost during each regeneration (due to breakage). After every year, top up of columns with 10% is required (Remco engineering, water systems and tools)

Hence, replenishment every year = $(10 \times 26.14)/100 = 2.614 \text{ ft}^3$

6.2.2.4.1 Estimation of cost

The cost of ion exchange is as follows:

Cost of resin (@ 8870 per ft^3)

Thus, cost of replenishment every year = $2.613 \times \text{Rs } 8870 = \text{Rs } 23177$

Components	Cost (in Rupees)
Installation cost	231720
Chemical cost	3174
Maintenance cost	23177
Total Investment	258071

Table 6.2 Cost details of Ion exchange

6.2.2.4.2 Savings in ion exchange

Recovery of Nickel and recycling to Nickel plating bath (recovery rate >97%) and the balance 3% requires treatment (Source: COINDS).

Mass of Nickel sulphate lost in a year = $2.32 \times 300 = 696 \text{ kg/year}$

Mass of nickel chloride lost in a year = $0.186 \times 300 = 55.8 \text{ kg/ year}$

Mass of boric acid lost per year = $0.107 \times 300 = 32.1 \text{ kg/ year}$

Hence, a large amount of money can be saved. Ion exchange has 97% recovery rate

Reduction in nickel sulphate = $696 \times 0.03 = 20.88 \text{ kg/year}$

Reduction in nickel chloride = $55.8 \times 0.03 = 1.674 \text{ kg/year}$

Reduction in Boric acid = $32.1 \times 0.03 = 0.963 \text{ kg/year}$

Hence, savings in cost of chemicals are as follows,

Savings of chemical = Cost of chemical (in Rs) x amount of chemical recovered

Savings of Nickel sulphate per year = Rs178 x 675.12 = Rs 120171

Savings of Nickel chloride per year = Rs 360 x 54.12 = Rs 19485

Savings of Boric Acid per year = Rs 70 x 31.13 = Rs 2179

Total savings = Rs 141835

6.2.2.4.3 Payback period of Ion exchange

Amount saved per day from savings (assuming 300 working days) = $141835/300$
= Rs 473

Payback period for the equipment cost = $231720/463 = 489.8$ days ~ 490 days
= 19.6 months (300 working days)

Thus, payback period is 20 months (assuming 300 working days).

After the payback period of approximately 1 year and 8 months, the plating unit will be able to save some amount at the end of 2 years as shown:

Savings at the end of 2nd year = 110 days x Rs 473 = Rs 52030

Also, the cost of chemicals and maintenance for 2 years = $2 \times (3174 + 23177)$
= Rs 52702

Thus, at the end of 2nd year the cost of chemicals and maintenance is almost recovered (52702-52030= Rs 672)

At the end of 3rd year the savings will be = $141835 - (672 + 3174 + 23177)$
= Rs 114812

Thus, by installing Ion exchange system of recovery, the savings per year will be Rs 115484. Thus, this technique of ion exchange is feasible from both economic and environmental point of view.

Ion exchange method is economical for the recovery and recycling of wastewater. The advantage of this technique is that it can be applied to a variety of metals. Also, it helps in removal upto parts per million (ppm) levels.

6.2.2.5 Disadvantages of Ion exchange

- 1) The main disadvantage of using ion exchange resin is with regard to impurities that can cause problems. For instance some ions occurring naturally in water can foul the resin and lead to problems.
- 2) The ion exchange resin itself can sometimes become the source of contamination as the new ion exchange resin often has organic elements remaining in the resin beads after manufacturing.
- 3) It has high operating cost over long-term.

6.2.3 Reverse osmosis (RO) for recovery of chemicals

RO consists of a semi permeable membrane which selectively allows water to pass through it and restricts the entry of impurities. Reverse Osmosis is called so because the transfer is taking place against the concentration gradient as high pressure is applied over the solution.

Reverse osmosis is a pressure driven membrane separation process. In this process, the feed stream (rinse water) pumped in RO equipment and is kept under pressure and is separated into permeate stream and concentrate stream (chemicals).

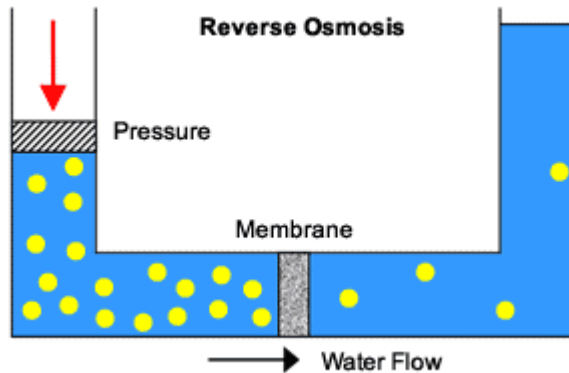


Figure 6.1 Process of Reverse Osmosis

(Source: Water filters and Purification equipment, Your Total water solutions)

6.2.3.1 Factors associated with performance of RO

It is evident the efficiency of RO process depends on the membrane performance. Membrane performance is characterized in terms of flux and rejection.

- a) Flux is the rate at which purified water permeates through membrane/unit area of membrane surface and is expressed as litres/m²hour.
- b) Rejection rate is the degree to which salts are prevented from passing through membrane and is given as:

$$\text{Rejection (\%)} = \frac{C_f - C_p}{C_f} \times 100 \text{ ----- (12)}$$

Where, C_f = concentration of feed stream

C_p = concentration of permeate stream

(Source: Metcalf and eddy)

- (i) Pressure - In general, both flux and rejection rate increases with the increase in operating pressure.
- (ii) Concentration – both flux and rejection rate decreases with the increase in feed concentration.
- (iii) Temperature - Flux increases with temperature, but rejection is temperature independent.

- (iv) Flow rate - The flow rate of feed should be tangential to the surface of membrane. The tangential flow should be maintained at enough level to prevent build up of rejected salts at the surface of membrane.

These units can treat larger volumes, making rinsing much easier, while recovering >95% of the nickel salts. While often more expensive than some evaporators, reverse osmosis (RO) units can produce a fairly concentrated 10-20 g/L product.

Spatz (1979) discussed the use of RO in the nickel plating industry to recover nickel from nickel plating bath rinse water. In this process, the permeate was recycled as rinse water, and the concentrate was recycled back to the plating bath. This allowed 95% recovery of the rinse water, and nickel consumption was significantly reduced.

6.2.3.2 Case study of Reverse Osmosis

The chemical recovery from reverse osmosis will be illustrated by taking a case study from a plating unit, performing nickel plating in Moradabad.

The wastewater coming out after 2 stage counter current rinsing operation has concentration 1025 mg/l and flow rate is 160 l/ day (values are taken from chapter-5).

The RO unit provides 95% recovery (R) and has rejection rate of 90% (r), thus other parameters were estimated below:

$$\text{Recovery rate, } R (\%) = (Q_P / Q_F) \times 100 \text{ ----- (13)}$$

Where, Q_P = flow rate of permeate, Q_F = flow rate of influent (wastewater)= 160 l/day

So, finding Q_P from equation 10 as,

$$Q_P = 0.95 \times 160 = 152 \text{ l/day}$$

Applying, mass balance to the RO system

$$Q_F = Q_P + Q_C \text{ ----- (14)}$$

Where, Q_C = flow rate of concentrate (chemicals in plating bath)

$$\text{Hence, } Q_C = 160 - 152 = 8 \text{ l/day}$$

Now, finding concentration of permeate using equation (12),

$$C_p = C_f (1 - r)$$

$$C_p = 1025 (1 - 0.9)$$

$$C_p = 102.5 \text{ mg/l}$$

Now to calculate the concentration of concentrate stream C_c .

By modifying the mass balance equation (11), we get,

$$Q_f C_f = Q_p C_p + Q_c C_c \text{ ----- (15)}$$

$$\text{Then, } C_c = \frac{Q_f C_f - Q_p C_p}{Q_c} \text{ ----- (16)}$$

Now putting respective values in equation (16)

$$C_c = \frac{(160 \times 1025) - (102.5 \times 152)}{8}$$

$$C_c = 18552.5 \text{ mg/l} = 18.55 \text{ g/l}$$

6.2.3.2.1 Estimate of cost

Filter cartridges need to be replaced in every 2 months

No. of cartridge replacement in a year = 6

Cost of filter cartridge (@ Rs 2200) = $6 \times 2200 = \text{Rs } 13200$

Membrane replacement is done in 3 years.

Electricity cost of Reverse osmosis can be estimated. The energy requirement for an RO Plant without any energy recovery is about 10 to 12 kWh per cubic meter of water (permeate) produced (Reverse osmosis plants, water and wastewater engineering).

Water produced in this case (Q_p) = 152 l/ day

Water produced in a year (assuming 300 working days) = $152 \times 300 = 45600 \text{ l/year}$
 $= 45.6 \text{ m}^3$

Cost of electricity per year (@ Rs 4.65 per unit) = $12 \times 4.65 \times 45.6 = \text{Rs } 2550$

Total energy cost and maintenance cost /year = $2550 + 13200 = \text{Rs } 15750$

Components	Cost (in Rupees)
Reverse Osmosis system	133020
energy cost and maintenance /year	15750
Total Investment	148770

Table 6.3 Cost details of Reverse osmosis system

6.2.3.2.2 Savings by using Reverse Osmosis

The chemicals can be recycled to bath after the process of evaporation.

The loss of chemicals in drag out is as following (similar to atmospheric evaporator case study):

Mass of Nickel sulphate lost in a year = $2.32 \times 300 = 696$ kg/year

Mass of nickel chloride lost in a year = $0.186 \times 300 = 55.8$ kg/ year

Mass of boric acid lost per year = $0.107 \times 300 = 32.1$ kg/ year

Hence, a large amount of money can be saved. RO has 95% recovery rate

Reduction in nickel sulphate = $696 \times 0.05 = 34.8$ kg/year

Reduction in nickel chloride = $55.8 \times 0.05 = 2.79$ kg/year

Reduction in Boric acid = $32.1 \times 0.05 = 1.605$ kg/year

Hence, savings in cost of chemicals are as follows,

Savings of chemical = Cost of chemical (in Rs) x amount of chemical recovered

Savings of Nickel sulphate per year = $Rs178 \times 661 = Rs 117658$

Savings of Nickel chloride per year = $53.1 \times Rs 360 = Rs 19084$

Savings of Boric Acid per year = $30.49 \times Rs 70 = Rs 2134$

Total savings = Rs 138876

6.2.3.3 Payback period of Reverse Osmosis

Amount saved per day from savings (assuming 300 working days) = $138876/300$
= Rs 463

Payback period for the equipment cost = $133020/463 = 287.3$ days ~ 287 days
= 11.4 months (300 working days)

Thus, payback period is 11.4 months (assuming 300 working days).

The cost of electricity per year = Rs 15750

After the payback period of approximately 1 year, the plating unit will be able to compensate the electricity cost of 2 years and afterwards, will be able to save money as = $138876 - (2 \times 15750) = \text{Rs } 107376$

In 3rd year the total savings will be = $(107376 + 138876) - 15750 = \text{Rs } 230502$

The amount saved at the end of 3rd year will be enough for the replacement of membrane and for the treatment of permeate water having concentration 102.5 mg/l and flow rate as 152 l/day.

Savings per year = Rs $(138876 - 15750) = \text{Rs } 123126$.

Thus, both economically and from environmental point of view, RO technique proved to be useful for the above case study.

6.2.3.3 Disadvantages of RO system

- a) RO operates in pH range of 2-11, so highly acidic or highly basic in nature chemicals cannot be recovered.
- b) RO is incapable of concentrating solutions to very high concentrations. Thus, a small evaporator is required to close the loop.
- c) Certain species which are small non-ionized molecules (Sodium, brightener) are not completely rejected.
- d) Membrane performance generally degrades with time requiring periodic replacement of membrane.

6.2.4 Electro Dialysis

In electro dialysis process, the ionic component from wastewater is separated through the use of semi-permeable ion-selective membranes. It has many applications in recovery.

6.2.4.1 Principle of electro dialysis

When electric current is passed through the solution it causes a migration of cation towards negative electrode and migration of anions towards positive electrode. The equipment consists of alternate spacing of cation and anion permeable membranes. It consists of pump for pumping wastewater in the electro dialysis unit. There are number of collecting trays to collect the dilute and concentrated streams. The concentrated stream consists of 2 streams:

- Anode rinse – containing positively charged ions in concentrate (Ni^{2+}).
- Cathode rinse –containing negatively charged ions as concentrate (SO_4^{2-}).

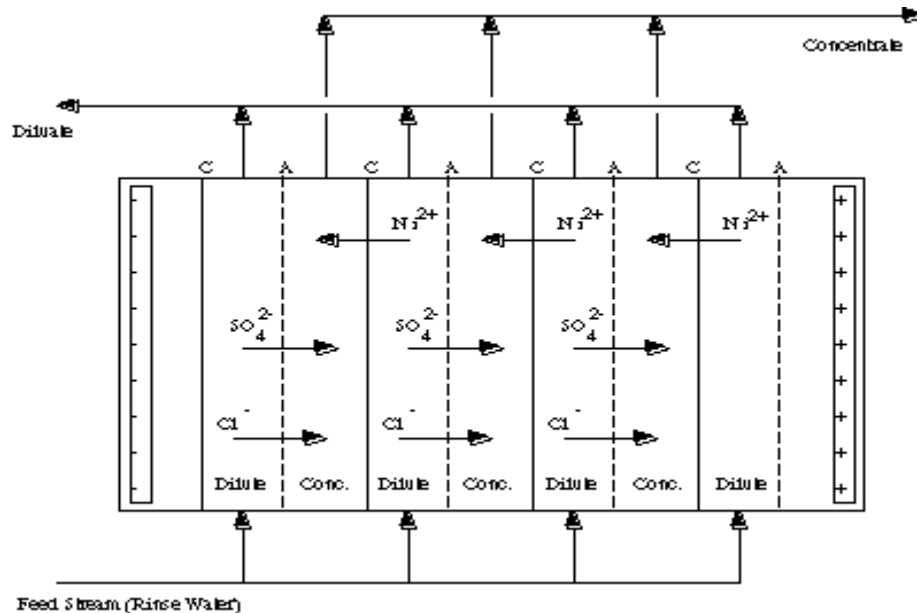


FIGURE 6.2 showing the chemical recovery of nickel from Watt's plating bath solution by Electro dialysis

(Source: Pollution prevention and control technologies for plating operations, National metal finishing Resource centre)

Wastewater is pumped in electro dialysis cells as shown in figure 2. When electric current is passed through the wastewater, the formation of cations (Ni^{2+}) and anions (SO_4^{2-}) takes place which migrates to cathode and anode respectively. The ions get separated by cation and anion selective permeable membranes. This causes the formation of 3 streams:

- a) Cathode stream
- b) Anode stream
- c) Dilute stream – containing water

The 3 streams are collected in different trays, which can be recycled to plating bath.

6.2.4.2 Factors affecting Electro dialysis

However, the removal of salts depends on following factors:

- i. Amount of electricity passed through the solution
- ii. Type and amount of ions
- iii. Temperature of wastewater
- iv. Selectivity of membrane
- v. Flow rate of wastewater

6.2.4.3 Case study of Electro dialysis

The chemical recovery from electro dialysis will be depicted by taking a case study from a plating unit, performing nickel plating in Moradabad.

The wastewater coming out after 2 stage counter current rinsing operation has concentration 1025 mg/l and flow rate is 160 l/ day (values taken from Chapter-5)

The current required for electro dialysis can be estimated using Faraday's laws of electro dialysis. The number of gram equivalents removed per unit time is given by:

$$\text{Gram eq/ unit time} = QNy \text{ ----- (17)}$$

Where, Q = flow rate in litres/second

N = normality of solution, eq/l

y = electrolyte removal as a fraction

The corresponding expression for current for a stack of membranes is given by:

$$I = \frac{FQNY}{nE_C} \text{ ----- (18)}$$

Where, I = current in Ampere

F = faraday's constant, 96485 A.s/eq

n = number of cells in a stack

E_C = current efficiency expressed as a fraction

(Source: Metcalf and Eddy)

Cation and anion concentration = 0.96 g-eq/l

Now, efficiency of salt removal of electro dialysis = 50%

The current efficiency = 90%

Resistance = 7 ohms

No. of cells in stack (n) = 25

6.2.4.3.1 Cost of Electro dialysis

Calculating the current required using equation (18)

$$I = \frac{96485 \times 160 \times 0.96 \times 0.5}{25 \times 0.90 \times 8 \times 3600}$$

$$I = 11.43 \text{ A}$$

Determining the power (P) required

$$P = R (I)^2$$

$$P = 7 \times (11.43)^2$$

$$P = 914.5 \text{ W} = 0.914 \text{ kW}$$

$$\text{Power requirement for a year} = 0.914 \times 8 \times 300 = 2194 \text{ units}$$

$$\text{Energy cost} = 2194 \times \text{Rs } 4.65 = \text{Rs } 10202$$

Components	Cost (in Rupees)
Electro dialysis system	354720
energy cost and maintenance /year	10202
Total Investment	364922

Table 6.4 Cost details of Electro-dialysis system

6.2.4.3.2 Savings by using electro dialysis

The drag-out losses are as follows:

$$\text{Mass of Nickel sulphate lost in a year} = 2.32 \times 300 = 696 \text{ kg/year}$$

$$\text{Mass of nickel chloride lost in a year} = 0.186 \times 300 = 55.8 \text{ kg/ year}$$

$$\text{Mass of boric acid lost per year} = 0.107 \times 300 = 32.1 \text{ kg/ year}$$

The salt removal efficiency of electro dialysis equipment is 50%

$$\text{Savings of Nickel sulphate per year} = \text{Rs } 178 \times 348 = \text{Rs } 61944$$

$$\text{Savings of Nickel chloride per year} = \text{Rs } 360 \times 27.9 = \text{Rs } 10044$$

$$\text{Savings of Boric Acid per year} = \text{Rs } 70 \times 16.05 = \text{Rs } 1123.5$$

$$\text{Total savings per year} = \text{Rs } 73111$$

6.2.4.3.3 Payback period of Electro dialysis equipment

$$\begin{aligned} \text{Amount saved per day from savings (assuming 300 working days)} &= 73111/300 \\ &= \text{Rs } 244 \end{aligned}$$

$$\begin{aligned} \text{Payback period for the equipment cost} &= 354720/244 = 1453.7 \text{ days} \sim 1454 \text{ days} \\ &= 58.16 \text{ months (300 working days)} \end{aligned}$$

Thus, payback period is 58 months (assuming 300 working days). Thus it will be approximately equivalent to 4 years and 10 months.

At the end of 5 years the savings will be = Rs 244 x 50 = Rs 12,200

Now, calculating savings in energy consumption,

The cost of electricity per year = Rs 10202

Cost of electricity for 6 years = Rs 10202 x 6 = Rs 61212

The savings at the end of 6th year will be = Rs (12,200+73111) – Rs 61212
= Rs 24100

Afterwards, the savings per year will be = 73111 – 10202 = Rs 62909

The technique of electro dialysis has a long payback period of 4 years and 10 months and the salt recovery is also 50%. So, this technique of recovery is not fit for the above plating unit.

6.2.4.4 Disadvantages of Electro dialysis

- a) Organic matter, colloids and SiO₂ are not removed by Electro Dialysis system.
- b) Feed water pre-treatment is necessary to prevent Electro Dialysis stacks fouling.
- c) Elaborate controls are required, and keeping them at optimum condition could be difficult.
- d) Selection of materials of construction for membranes and stack is important to ensure compatibility with the feed stream.

6.3 Overall comparison of chemical recovery techniques

Technique	Cost of Equipment (in Rs)	Recovery efficiency (in %)	Payback period (in months, assuming 300 working days)	Savings/year (in Rs)
Evaporation	117391	90	11	-
Ion Exchange	231720	97	20	115484

Reverse Osmosis	133020	95	12	123126
Electro Dialysis	354720	50	58	62909

Table 6.5 Comparison of different techniques of chemical/metal recovery with respect to efficiency and payback period.

It was found from the case study done at Moradabad, that evaporation technique is not feasible due to high operating costs (electricity charges were more than savings per year)

Though the cost of the machine is least, but the operating cost (electricity charges Rs145824 per year) is quite high as compared to other techniques (RO and Electro dialysis). Thus, in totality the running cost of equipment is less than the savings done by the equipment. Therefore, the expenditure or amount of money used in operation will be always on the higher side for the above discussed plating unit.

Suitable condition for the use of evaporator

The technique may be suitable for recovery of metals/ chemicals which are expensive (e.g. Gold, Silver etc).

The comparative data from Table 6.5 indicated that payback period of electro dialysis is quite long (4 years, 10 months), and recovery of salt is also 50% also. Thus, this technique may prove costlier and wastewater still requires effluent treatment.

The performance of ion exchange and RO system was found to be similar, with respect to savings per annum (ion exchange – Rs 115484, RO – Rs 123126) and efficiency (Ion exchange- 97%, RO- 95%). The payback period of RO system (12 months) is significantly less than Ion exchange (20 months), but, the drawbacks of RO system were its incapability to concentrate wastewater to high concentrated chemicals (needs evaporation).

Also, the use of RO system was restricted to pH range of 2-11 only. Therefore, it can be concluded that the ion exchange method is superior to other techniques of chemical recovery, which was established by the given case study done at Moradabad

Table 6.6 Types of plating and suitable technique for recovery of metal

Methods/ Techniques	Cyanide Silver plating	Acid Copper Plating	Nickel Plating	Decorative Chrome Plating	Hard Chromium Plating	Cyanide Zinc Plating	Cadmium Plating	Copper Plating
Ion- Exchange*		Yes	Yes	Yes	Yes			Yes
Reverse Osmosis	Yes		Yes			Yes	Yes	Yes
Electro- Dialysis*			Yes	Yes	Yes			
Evaporation*	Yes		Yes	Yes		Yes	Yes	
Typical Recovery Efficiency	>99%	80- 90%	98%	98%	95%	70%	70%	98%

*Source: UNEP: "Environmental Aspects of Metal Finishing Industry, A Technical Guide, "Paris, 1993

Chapter 7

Summary and Conclusion

In the study, survey was done in organized sector of Electroplating Industry in Moradabad (U.P.). The main focus of project centers on the electroplating industry and its environmental concerns.

The electroplaters are found in entire country with significant proportion in Punjab, Haryana and U.P. so, Moradabad was selected as the study area, having variety of electroplaters in both organized as well as unorganized sector. So, therefore, with the help of a case study an attempt was made to investigate the feasibility of introducing waste minimization and chemical recovery techniques.

The report gives the idea about the typical chemicals used in different metal plating with their environmental concerns.

Waste minimization encompasses the techniques to minimize the resources viz. counter-current and spray rinsing techniques. Reduction of resources (water for rinsing) was illustrated with the help of case study (done at Moradabad). The reduction in water for rinsing will directly reduce the toxic metal/hazardous waste discharged into the water bodies

By using 2 stage counter-current rinsing it was found that the consumption of rinse water reduced from 2250 l/day to 160 l /day, which is almost 93% reduction in the consumption of rinse water. The spray rinsing technique reduces the water consumption from 2250l/day to 282 l/day. This is a remarkable achievement both in terms of environmental and economic point of view.

On comparison, it was found that counter current system not only reduces the consumption of water more effectively than spray rinsing but, also operating and maintenance cost is cheaper than spray rinsing in given case study. Thus, counter current technique should be used instead of spray rinsing for the above mentioned electroplating unit.

Waste minimization procedure is followed by chemical recovery. Chemicals are present in wastewater after rinsing as drag out losses. There are many techniques for chemical recovery in electroplating. In this project work, only 4 techniques were discussed in detail namely, Evaporation, Ion-exchange, Reverse osmosis and Electro dialysis. The comparative study table has been done in Chapter 6 (refer Table 6.5)

It was found from the case study done at Moradabad, that evaporation technique was not feasible for the given unit, due to high operating costs (electricity charges were more than savings per year). The technique of Ion exchange was found to be the most feasible technique for chemical recovery, with minimum waste generation and optimized chemical recovery as compared to the other techniques (RO, Evaporation and Electro dialysis).

According to the COINDS, CPCB have also conducted studies on chemical recovery. On comparing the results of the given study, and COINDS, it was found that Ion exchange is the most appropriate technique for chemical recovery.

The results are formed on theoretical calculations from the data obtained from the plating unit in Moradabad. The actual performance of all the equipments will have to be determined from pilot tests. In practice, due to leakage and other operational and design limitations, the required volume of resin in ion exchange will be usually higher than computed exchange capacity.

The project report lacks the energy conservation in the industry, which could not be performed due to project constraints.

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