Waste Reduction Strategies for the Printed Circuit Board Industry

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EXECUTIVE SUMMARY

This document contains a brief summary of the first six chapters contained in the original report to the California Department of Health Services, followed by the complete chapters 7, 8 and references. It is hoped that this condensed format will make the study more widely available, especially to decision makers in the industries concerned.

The major conclusion of this study is that significant reductions in the generation of hazardous metal wastes are feasible, both from a technical and an economic point of view, using techniques ranging from simple water conservation devices to integrated zero-sludge, resource recycling systems.

For printed circuit board plants with a daily process water flow of 100,000 gallons or more, integrated zero-sludge, resource recycling systems are more economical than conventional sludge based systems. The higher capital costs of the zero-sludge systems are more than offset by savings in sludge transport and disposal costs, water costs (both for water intake and for discharge to sewer), and labor costs. As these latter costs continue to rise, zero-sludge systems will provide even greater savings over conventional systems.

Furthermore, zero-sludge systems provide additional, harder to quantify cost savings associated with:

- protection against further restrictions on the land disposal of toxic wastes
- reduced insurance rates
- recovered metals and process chemicals
- protection from the legal liability, and vulnerability of corporate image associated with sludge transport and disposal.

Further conclusions are:

**Waste Generation and Management**

1. The major sources of hazardous heavy metal wastes generated
by the printed circuit board industry are from the plating and etching processes employed. Large quantities of contaminated rinse water and drag-out residue are generated in the processes that cannot be discharged directly to sewer systems. A large circuit plant may use and discharge around 200,000 gallons of water per day. Most firms in the industry have resorted to conventional precipitation/sedimentation (sludge-based) treatment systems to meet pretreatment standards for discharge to publicly owned treatment works.

2. Conventional sludge-based treatment systems generate large quantities of heavy metal sludge for disposal. A typical small printed circuit board plant may generate about 6 tons per year of copper sludge alone and a large plant can generate more than 100 tons per year.

3. Printed circuit board firms generated anywhere from about 250 pounds to about 4,000 tons of total hazardous waste per year in 1985, the majority being sludges and liquids containing heavy metals. From available data, it is impossible to determine the total amount of hazardous heavy metal wastes generated each year by the industry as a whole, but 57 companies reporting offsite shipments generated about 14,000 tons of heavy metal waste in 1985 out of total hazardous waste generation of about 20,000 tons.

4. Most of the heavy metal waste streams generated by this industry are sent offsite for disposal in landfills or surface impoundments. Of the 20,000 tons of hazardous waste sent offsite for management in 1985 by the 57 firms reporting manifest information, over 15,000 tons were managed by some form of land-based disposal or treatment.

5. Waste reduction measures implemented by the printed circuit board industry are in an early stage and to date are primarily improvements to conventional sludge-based pretreatment systems to reduce the volume of sludge generated for disposal. Other simple measures, such as installation of water conservation devices, have been implemented, and there are some simple metal recovery devices that have been installed.

Economic and Institutional Factors

6. There are economic barriers in the printed circuit board industry to the implementation of waste reduction measures requiring significant capital investment:

   - The industry has been in a slump from which it is slowly emerging and is still troubled by increased competition from foreign countries.
Most firms in the industry are small, having little surplus capital for investment in waste reduction. Most surplus capital in the industry is spent on upgrading manufacturing technologies to produce increasingly sophisticated circuit boards in order to remain profitable.

The industry is highly capital intensive, with fixed costs being the major portion of manufacturing costs. This creates a strong disincentive for investment in equipment for waste reduction during industry slumps when production is only a fraction of capacity. This is particularly true for waste reduction measures that require significant capital investments even if they will ultimately pay for themselves in operating cost savings.

7. The fragmentation of the industry into hundreds of small firms with loose industry organization makes the widespread introduction of new waste reduction technologies difficult and allows many firms to escape the regulatory pressures that will eventually demand waste recovery.

Regulatory and Legal Factors

8. The printed circuit board industry has been caught in a regulatory squeeze as pretreatment standards for discharge of waste water have tightened and land disposal restrictions for heavy metal wastes have been implemented. The impact of this regulatory squeeze is heightened by the dramatic increases in hazardous waste land disposal prices and increasing water costs (both for water intake and for discharge to sewer). As a result, waste management is a high-priority issue in the industry creating a receptive atmosphere for implementation of waste reduction measures.

9. Under the Department of Health Services hazardous waste regulations, printed circuit board firms using conventional sludge-based waste water pretreatment processes may be required to obtain hazardous waste TS&D permits or secure exemptions based on a showing of adequate regulation through pretreatment permits. The prospect of having to obtain a TS&D permit is a strong incentive for the implementation of zero-discharge waste recovery measures to avoid hazardous waste generation. At present, exemptions from the TS&D permit requirement are being issued slowly at best, and many firms are ignoring the requirement.

10. If the requirement for hazardous waste TS&D permits is applied to onsite recycling facilities in the printed circuit board industry, waste reduction would be
discouraged. The hazardous waste recycling exemption for onsite recycling should be liberally applied to encourage waste reduction.

11. Concerns over future liability for hazardous waste disposal and the expense and unavailability of environmental impairment liability insurance are also an important driving force for waste reduction in the industry.

Technologies for Waste Reduction

12. There are several simple housekeeping and waste stream segregation approaches that are the most cost-effective waste reduction measures for implementation in the printed circuit board industry. Implementation of these, however, would still leave conventional sludge-based treatment as a major source of hazardous waste generation in the industry.

13. Process changes for waste reduction exist, such as the substitution of sulfuric acid/hydrogen peroxide etch for the typical copper etch, but other than this example alternative process chemistries have not proven too popular in the industry since they are often too sensitive to equipment and operating parameters.

14. There are several proven technologies for recycling heavy metals that can be applied in the printed circuit board industry for specific waste streams. These technologies include electrolytic recovery, ion-exchange, and evaporative recovery, each of which works quite well alone for a specific waste stream composition and concentration. There is a very positive attitude in the industry toward use of these technologies.

15. Although none of the recovery technologies alone is the complete answer for waste reduction in the industry, larger firms should be capable of implementing integrated zero-sludge recovery systems incorporating several specific recovery technologies working together. Such a system, as will be demonstrated by TRSI in a Phase III DOHS demonstration project, can completely eliminate generation of hazardous heavy metal sludges and recycle over 90% of process water.

16. Smaller firms will probably want to implement waste reduction measures stepwise by incorporating recovery technologies on selected waste streams and upgrading their conventional sludge-based treatment systems to reduce sludge generation.

17. A preliminary economic comparison of an integrated zero-discharge recovery system with conventional sludge-based treatment for a large printed circuit board
firm shows that the recovery system is competitive with the sludge-based system without any credit for recycled metals or reduced liabilities. If the rates for sludge disposal and water (in and out) continue to increase, smaller firms may also find such an integrated system cost-effective.

Demonstration of Waste Reduction Technologies

18. A frequently heard complaint from printed circuit board industry executives is that regulatory agencies do not provide sufficient technical guidance on alternatives to waste management practices that are being restricted by regulations. The demonstration of waste reduction technologies, as with the Phase III grant recently awarded to TRSI, should be of great benefit to the industry.

19. Because of the economic and institutional impediments to the implementation of waste reduction measures in the printed circuit board industry, the Department should consider further incentives in addition to the demonstration program. Financial incentives and technical assistance programs are justified in this industry because of the overall benefits of waste reduction to society and because of the importance of the industry as the supplier of building blocks for the electronics industry and defense systems.
7. TECHNOLOGIES AND STRATEGIES FOR WASTE REDUCTION AND RECYCLING

This section of the report examines three important areas of development regarding waste management for the Printed Circuit Board Industry. It also attempts to make some preliminary cost comparisons for recovery systems versus conventional sludge-based treatment of metal bearing wastes. The three areas for review are:

1. In-plant changes and process modifications
2. Resource recovery and recycling technologies
3. Integrated waste reduction strategies

7.1 In-Plant Changes and Process Modifications

7.1.1 Waste Audit

Minimization of the levels of treatable waste is a critical requirement for optimizing operating costs of existing waste management systems and is also a key factor in the design of new waste treatment installations. Two main approaches have been identified. The first is generally referred to as a waste audit or plant assessment and consists of reviewing current manufacturing practices and identifying in-plant or housekeeping changes which might reduce the volumes of treatable waste. The other major development in this area has been the search for alternative processes which eliminate or reduce toxicity. While most of the efforts in this area have been directed towards the more toxic metal finishing processes, some applications in the printed circuit board industry have also been suggested.

7.1.2 In-Plant Changes

The most promising area where in-plant operational or housekeeping changes can make a significant impact on bottom line waste management costs is in rinsing practices (24). Traditionally, the metal finishing industry and to a lesser extent the printed circuit board industry, have used large volumes of rinsewater with the dual aim of improving product quality and diluting the concentration of toxics in the effluent stream. More recently, with the pressure to minimize water usage and with the costs of waste management being directly related to the volume of process water usage, there has been a trend towards more efficient usage of rinse water. One result has been an increasing use of process control, particularly the use of conductivity and flow controls. Another approach has been the increasing trend
toward spray rinsing techniques. The introduction of a spray rinse prior to a conventional countercurrent rinse has the attractive feature of providing a low volume, high concentration waste stream readily amenable to treatment by selected recovery techniques.

7.1.3 Process Changes

Traditionally, the manufacturers and suppliers of plating and process chemicals have also been faced with supplying waste management expertise and even treatment services to their clients. Consequently these groups have also headed the search for less toxic and more readily waste treatable process chemistries (16). In the metal finishing industry the main candidates have included the replacement of chromium (VI) with Cr(III), the development of cyanide-free baths and the search for alternatives to cadmium. In the printed circuit board industry the major search has been for etchant processes to replace the current Cu(II)-ferric chloride or ammonia based systems and also the search for alternatives to lead borofluoride for solder plating. In the area of etchant process chemistry, sulfuric acid-hydrogen peroxide is finding increasing acceptance, particularly for micro-etch application, while sulfonic acid based baths have recently been introduced for tin/lead processes.

One general comment, however, on the subject of alternate process chemistries which resulted from the industry survey was that these newer chemistries often require more careful process control and in some cases involve equipment changes. The resources to support these changes are often only to be found in the larger plants. Smaller operations, on the other hand, are more likely to retain established process technologies and absorb the subsequent higher waste treatment costs. This opinion was also reinforced by the delicate state of the printed circuit board market. Companies already struggling hard to maintain their market share would be reluctant to commit to changes in their manufacturing processes with the possibility of even temporary interruption of production or minor deterioration in product quality.

7.2 Resource Recovery and Recycling Technologies

The concept of resource recovery in hazardous waste management is not new. The chemical process industry has long been applying the approach of use, reuse, recovery and recycling to handle a large part of its hazardous wastes. Traditionally, however, industries generating metal wastes have tended to rely on offsite disposal because of the technical and economic barriers to adopting metal recovery processes and the attraction of the lower-priced alternative. While a large number of physical, chemical and biological techniques have been proposed for the treatment and recovery of hazardous materials (17-31), only a limited number have demonstrated practical utility and reliability within the circuit board industry.
The techniques which have either demonstrated applicability in the industry or show potential for future use include ion-exchange, electrolysis, membrane separation technologies including electrodialysis, reverse osmosis and Donnan dialysis/coupled transport, ultrafiltration and cross-flow microfiltration, evaporation, adsorption, solvent extraction, distillation, thermal decomposition and biotechnology. Some comments on the principles and potential application of the more relevant techniques are included below.

7.2.1 Ion-Exchange

Ion-exchange has been used in various forms for waste recovery for more than 20 years (19), but it is only in recent years with the developments in low-cost process control technology, that the technique has become economically viable. Ion-exchange materials occur in both natural and synthetic forms. Naturally occurring ion-exchange materials include clays, zeolites, peats and even some plants, such as the water hyacinth. Synthetic ion-exchange resins are most commonly a solid polymeric substrate with the active site linked to the resin. This site can exchange either cations or anions, according to the exchanger type. Typically, the resin might exchange site-bound sodium for heavy metal cations or hydroxide ions for either anions or complexed metal anionic species. Ion-exchangers can also be fabricated into cloth, sheets or membranes where the active ion-exchanger is either physically trapped in the pores or is chemically bonded (e.g., by radiation grafting) to the supporting matrix. The most practical type of resins for waste recycling applications in the printed circuit board industry are the solid polymeric gel type, which offer a range of complexing ability.

Figure 7.1 shows a general process flow schematic diagram for the application of ion-exchange systems for metal recovery. The low-level metal streams from the process rinse operations are first filtered through an activated carbon filtration unit that removes traces of organic impurities such as proprietary bath additives. The filtered process stream is then passed through the ion-exchange columns, which are usually operated with two in series, the first acting as a collector and the second as a guard column. In some cases a third standby column is introduced as follows: When the first column is fully loaded the process stream is switched to the guard (second) column and the standby (third) column becomes the guard while the first column undergoes regeneration. The regeneration process involves washing the column with a stream of reagent (the eluent) that displaces the metal from the ion-exchange resin. The resulting metal concentrate solution (the eluate) typically ranges from 1-30 grams per liter and can, in some instances, be recycled directly to the process bath. Alternatively, the metals can be removed in a separate treatment step. For example they can be recovered in the form of a metallic sheet through electrolysis.
Figure 7.2 shows a process flow schematic for the treatment of a copper rinse stream. The input stream composition would typically range from 50 to 500 parts per million in copper. In the case of acid copper recovery systems, dilute sulfuric acid is used as an eluent to wash the ion-exchange column; for chelated copper recovery which uses an anion-exchanger for collection of the copper chelate anionic complex, a 10% brine solution is used for elution. Figure 7.2 also shows the use of an electrowinning cell to recover copper from the ion-exchange eluate (see also Section 7.3).

The effluent stream after ion-exchange can either be pH-adjusted and discharged directly to the sewage system or it can be further treated with a demineralization step (mixed ion-exchange process or reverse osmosis) to remove the traces of inert salts, usually sodium and chloride, which are generated in the ion-exchange elution process. The effluent from the latter process is high-purity, deionized water—a valuable commodity which can be recycled directly to the manufacturing process.

The major advantages of the ion-exchange technique:

1. Very effective in treating waste streams to part per billion range
2. Operates most effectively on low concentration process streams—for most competing technologies the reverse is true
3. Capable of treating cations, anions, and anionic complexes (i.e., complexed metals)
4. Capable of treating most metals (apart from Cr) of environmental significance
5. Regenerative process—provides a clean, concentrated process stream for recycling or metal recovery

The major drawbacks of the technique:

1. Process streams need chemical pre-processing, filtration, and pH control
2. Works best on segregated waste streams, not mixed metals
3. Requires regeneration to capture pollutant
4. Upper concentration limit for process stream
5. High capital cost

In summary, ion-exchange shows great promise for much wider application in hazardous waste management as the focal technique in a treatment system supported by ancillary recovery techniques such as electrolytic or evaporative treatment.
Fig. 7.1 SIMPLIFIED ION EXCHANGE SYSTEM
Fig. 7.2  COPPER RECOVERY USING ION EXCHANGE
7.2.2 Electrolytic Recovery Systems

Electrolytic recovery processes show tremendous promise for solving a major portion of the heavy metal waste management problems for a wide range of industries (18). The advances in electrochemical engineering which have occurred over the past two decades have resulted in the development of a spectrum of electrochemical reactor designs that can handle a wide range of pollution problems including metal recovery, detoxification of chemical wastes and removal/modification of organic substances.

Electrochemical reactors are generally comprised of a cell chamber or body, and a pair of electrodes (cathode and anode), of which one is usually the active working electrode and one is passive. In some designs there is a separator to isolate the anode and cathode cell compartments. The key engineering features of any cell are:

1. The hydrodynamic characteristics, or the means used to move the process stream through the cell and ensure transport of the metal ions to the working electrode

2. The current/potential distribution at the working electrode which in turn is related to the overall efficiency of the electrode process

The hydrodynamic mass-transport of metal ions in solution is controlled by the working electrode design (either high or low surface area), the design of the cell design and by the method of feeding the process solution (stirring, pumping, gravity flow, etc.). The current/potential distribution, which governs the selectivity and the efficiency of the desired process, is similarly controlled by working electrode design, geometry and material, by cell geometry, and by the conductivity of the process stream.

While a detailed discussion of electrochemical engineering principles is beyond the scope of this report, one key factor emerges that appears to have been overlooked by many of the companies producing commercial reactor systems. This is the fact that waste concentrations range from parts per billion up to hundreds of grams per liter, and that a variety of process media must be considered including air, water and organic solvents. For any given process or application, an optimum design of electrochemical reactor exists. Conversely, no single design of electrochemical reactor appears capable of handling all waste recovery problems. More realistically it seems that a spectrum of electrochemical reactor designs will be required.

Two important applications of electrochemical reactors in waste recovery can illustrate this point. The first relates to the recovery of metals from process rinse streams (Figure 7.3). Here
the process stream usually comprises a low metal concentration (up to 500 parts per million) and low solution conductivity. The appropriate reactor design utilizes a high surface area or high performance cathode, a low inter-electrode gap to minimize ohmic solution losses, and high mass transport. In contrast, the recovery of metals from spent process baths, etchant processes, or ion-exchange eluate, involves metal concentrations in the grams per liter range with high background electrolyte conductivity. For this application an electrowinning cell design is appropriate, which typically might be comprised of a planar cathode in a cell with an isolated membrane anode compartment (Figures 7.4 a,b, and c).

The major advantages of electrolytic recovery:

1. The technique is familiar to printed circuit board manufacturers (and electroplaters)
2. The systems are usually low cost and have minimal maintenance requirements
3. Offers a very wide, dynamic range of application, including metals, metal complexes, cyanides, and some organics
4. Can handle a broad spectrum of concentrations from low ppm up to grams per liter
5. Wide range of cell designs are available
6. Control requirements are relatively simple

The disadvantages:

1. Low concentration applications require process modifications
2. Best suited to single metal point source streams
3. Best suited to noble, electropositive metals, which covers all metals of environmental importance except Cr (and possibly Zn)
4. Interference from nitrates and some organics

In recent years, there have been enormous advances in electrochemical engineering with the result that modern high surface area cells are now many orders of magnitude more efficient than the earlier planar electrode cell designs. These advances translate directly to a lower capital and operating cost for a given level of metal removal with the result that electrolytic methods are now finding fairly wide application for a range of waste management problems. Electrolytic recovery shows particular promise for point source treatment and recovery of specific waste streams, as a technique that complements ion-exchange (recovery of metals from ion-exchange eluate), and as a potential technology for heavy metal sludge detoxification.
**Fig 7.3** ELECTROLYTIC RECOVERY FOR RINSE TREATMENT
7.2.3 Membrane Separation Technologies

The use of permeable or semipermeable membranes to separate the toxic components of chemical waste streams has attracted wide interest (23-26). Generally, these techniques can separate differing types of materials, solids and solutes, cations and anions from inert materials, organics from electrolytes, and traces of electrolytes from water. The separation process, common to all is achieved by inserting a membrane between the process or waste stream and a carrier or eluent stream. The mechanism required to effect the diffusion transport varies and ranges from simple concentration diffusion (dialysis) to a voltage gradient induced migration (electrodialysis).

Reverse Osmosis

In reverse osmosis (RO), separation of the impurities is achieved by applying a pressure on the process side of the membrane that is greater than the osmotic pressure caused by the dissolved materials in the solution. Crampton (24) has reviewed the application of cellulose acetate membranes for the concentration/recovery of plating bath drag out rinses. A schematic of the type of system described is shown in Figure 7.5. A wider survey of membrane types and their application to the treatment of various types of waste stream has been presented by Cartwright (25).

Electrodialysis

Three approaches to the use of electrodialysis have been described for the treatment of chemical waste streams: concentration-dilution (Figure 7.6), ion transfer, and electrolytic removal of impurities (23). The two former approaches have been used mostly for the recovery of chromic acid from dilute solutions, while the latter approach has been applied to the removal of impurity metals from spent process baths prior to recycling. Application of electrodialysis to the recovery of nickel from nickel plating rinse streams has also been reported (26).

Donnan Dialysis

Some recent work which shows promise for resource recycling and chemical recovery is the technique of Donnan Dialysis with coupled transport (27). The membrane barrier in this technique incorporates a liquid ion-exchanger trapped in the pores of the plastic matrix. The objective is to use an ion-selective ligand to allow selective transport of the pollutant metal across the boundary. To date, pilot application to chromium recovery has been demonstrated and work is in progress on a system to treat copper bearing waste streams.
Fig. 7.5  REVERSE OSMOSIS SYSTEM
Cross-Flow Microfiltration

Ultrafiltration and cross-flow microfiltration techniques have been used as a more efficient process for treatment of heavy metal sludges (28,29). Thus they are not strictly recovery technologies but their relevance to the present discussion is that they could provide a useful waste reduction approach, especially for small quantity generators who may have to rely on conventional treatment for handling part of their wastes.

A limitation to the wider use of membrane separation technologies would seem to be limited membrane lifetime and sensitivity to corrosive media. With the exception of cross flow microfiltration, a major drawback to the wider use of other membrane techniques is currently the process flow rate that can be achieved. In the case of reverse osmosis in which pore sizes as low as 0.001 microns are employed, very low flow rates from 10-25 gallons per sq. ft. of membrane area are typical. Similar constraints apply to electrodialysis.

Membrane separation technologies, however, still show great future promise as part of integrated waste management systems, especially where multicomponent waste streams containing both inorganic and organic components are concerned. Provided that the problems of membrane lifetime and limited flow characteristics can be overcome, then membrane separation techniques particularly when integrated with other recovery technologies should have major application for hazardous waste management.

7.2.4 Evaporative Recovery

Evaporative recovery is a widely used technique for waste minimization (22). It has some specific areas of application, especially for treatment and recovery of chromium VI wastes that are difficult to treat by other routes. Two main techniques have been developed, room temperature evaporative systems and high temperature evaporators. In the latter approach (Figure 7.7), salts are recovered from rinsewater by heating, usually under vacuum, to drive off the water. The condensed water can then be recycled to the process rinse stream. The concentrated salts are essentially desiccated plating bath solution. They can be stored and, after appropriate purification, fed back to the plating bath.

The major advantage of the evaporative recovery process is that it fills a gap in waste management techniques for chromium waste streams that are difficult to handle by other methods. Room temperature evaporation also has promise for application as a further pre-concentration step for spent process baths and as a precursor to a demineralization process.
**Fig 7.7 EVAPORATION SYSTEM**

**H = STEAM EVAPORATOR**
**S = SEPARATOR**
**C = CONDENSER**

- **PLATING**
- **RINSE TANKS**
- **RUNNING RINSE**
- **Waste Treatment**
- **Cooling Water**
- **Steam**
- **Concentrate Collection**
- **Vacuum Pump**
As a general waste management technique the major disadvantage of high temperature evaporative recovery is that it is highly energy intensive, so that careful minimization of rinse volumes are required. Furthermore, it generates a concentrated waste stream that usually requires further processing, since direct recycling to the process/plating bath is seldom possible.

7.2.5 Adsorption

The use of adsorbents, particularly activated carbon, is an established technique in the printed circuit board industry. Activated carbon adsorption is used, for example, to extract traces of organic additives, brighteners, etc., before removal of metals by ion-exchange or electrolytic recovery. These trace organics, which are invariably surface active agents, often have a deleterious effect on either ion-exchange resins or electrode surfaces. In addition, activated carbon adsorbers are used to remove traces of any solvents. They also have an important use in waste reduction by removing plating bath impurities in order to prolong plating bath life.

7.2.6 Biotechnology

The use of biological materials for the selective removal or detoxification of specific pollutants or metal ions has recently received considerable attention. Two specific areas of application show some promise for waste reduction or recovery in the circuit board industry. The first is the use of metal selective ligands as selective treatment agents for specific metals in the waste streams (30). The second area is the use of microbes to selectively remove or detoxify various metal pollutants (31).

In the former case, systems are presently in operation that incorporate metal-selective biological ligands adsorbed onto a solid matrix and used in a mode similar to an ion-exchange process. Little data is available on industrial application of these systems, and it is difficult to assess the advantages over conventional ion-exchange given the fact that most industry waste streams are already segregated thus eliminating the need for a highly selective treatment process. Developments in the latter area are far more speculative (31); some work has been carried out on the selective leaching of copper from ores and mining wastes while other research has shown that mercury(II) can be detoxified to mercury (0) metal by microbial action. Similar types of microbes could be used to treat copper waste streams but the major problem is the resistivity of the microbial species to the corrosive waste stream.
7.3 Integrated Waste Reduction Systems

A key point that emerges from the present survey and other waste management technology reviews, further supported by the project team's experience and industry contacts, is that there is no single technology that can solve all of the printed circuit board industry's total waste management problems. Instead, a realistic approach would seem to be one of integrating a number of proven treatment and recovery technologies along with an appropriate control and monitoring system. Furthermore, the optimum treatment strategy may well vary according to the type and size of the facility, and the type of manufactured product.

As was mentioned earlier, a prerequisite to the design of any waste treatment installation is the implementation of a plant-assessment study or waste audit. This provides a clear definition of the scope of the waste management problem and allows recommendations to be made for in-plant improvements to minimize levels of treatable waste prior to starting the system design.

Figure 7.8 is a schematic process flow diagram for an integrated zero-discharge waste management system for a printed circuit board plant (38). Dilute metal bearing waste streams (process rinses) are treated by ion-exchange while high concentration sources (spent process baths, etchants, spills etc.) are treated by an electrowinning process. The electrolytic recovery process is also used to treat the eluent from the ion-exchange columns after stripping. The treated waste stream, after leaving the ion-exchange, may be discharged directly to sewer after appropriate pH adjustment. Alternatively, a demineralization process can be used to remove the small amounts of inert salts which remain after ion-exchange treatment. The resulting high purity de-ionized water can be recycled to the manufacturing processes. Up to 95% of total process water can be recycled by this method. The electorecovery of the high metal concentration process sources and ion-exchange eluate is carried out in a cell known as an electrowinning cell which has stainless steel planar cathodes. The product from this operation is a metallic sheet of copper or nickel, etc., which can readily be peeled off the cathode. In some situations this metal can be reused, or alternatively it can be sold as nontoxic scrap.

The various segments of the overall waste management system, acid copper stream treatment, tin/lead stream treatment, final discharge control etc., can be packaged or skid mounted for ease of installation. The various segments of the waste treatment process are microprocessor controlled and can operate as individual (stand-alone) treatment units and can also be network linked to a central supervisory controller. A significant advance in the efficiency and reliability of such systems has been the use of distributed microprocessor control systems (made possible by advances in the printed circuit board industry). In
Fig. 7.8 Integrated Metal Waste Recovery System for a PCB Plant
this type of control scheme, a range of remote monitoring and control stations such as pH control, conductivity, flow control, and metals monitoring, are connected to a central supervising controller (which can be an inexpensive personal computer) to provide overall monitoring, control, and data recording.

7.4 Economics of Waste Management

A number of studies have examined the economics of waste management systems for the electronics, printed circuit board, metal finishing and some related industries (32-36). Several of these studies provide useful background data on specific treatment methodologies for various types and sizes of facility. To date there has been no economic comparison of the cost-benefits of the various waste management technologies and strategies for treatment of metal bearing waste streams. There are several barriers which make such a study difficult to implement:

1. At this stage of development there are only a few zero-sludge waste treatment systems installed in industry, and economic performance data is still being collected.

2. Many plants which operate conventional treatment systems do not have complete records on either capital or operating costs; often systems were installed in stages and details of real operating costs are difficult to define and even more difficult to obtain.

3. Costs of offsite waste disposal vary widely depending on location of plant and the type and volume of waste; small quantity generators usually pay higher charges, thus distorting average waste disposal costs.

4. It is difficult to identify suitable plants for comparison; in this study only two plants were examined. A more accurate comparison would examine several sizes and types of plant to assess sensitivity to economies of scale.

The studies which are relevant to the present project include a case study of existing treatment of wastes banned from landfill (37) and a detailed survey of the costs of conventional waste treatment for fourteen metal finishers and circuit board manufacturers in the Minneapolis area (36).
7.4.1 Preliminary Cost Comparison: Zero-Sludge Recovery System Versus Conventional Sludge-Based Treatment

The objective in this study was to compare the annual operating costs for waste management for two similar circuit board plants both in the medium to large segment of the industry. Data for the first plant was based on a TRSI installed recovery system (34) while the second plant was one studied in the industry survey carried out under the present contract. Waste treatment costs for this plant were also compared with the costs reported from other studies, particularly the data compiled by Duffy, Norgaard and Sandberg (36) and with other data from our industry survey.

In defining the parameters for cost comparison only current, quantifiable costs were used; no attempt was made to examine less tangible future costs such as increasing rates for sludge transport and water (both water inflow and outflow to sewer), legal liabilities, vulnerability of corporate image, or insurance costs. Based on our research, there is a clear need in California for a study which develops a more complete quantitative model of waste management costs for various types of heavy metal generating industries. Such a model would illustrate even more clearly the breakeven points at which the "zero-sludge" approach will become less expensive than conventional treatment.

Table 7.1 summarizes the data with a comparison of total installed cost (TIC) and total annual operating costs for the two plants and treatment approaches. The third column gives an average of the data compiled from the industry data in the present study along with the data from Duffy, Norgaard and Sandberg (36). The later were first weighted so that they all corresponded to a plant size of 100,000 gallons per day treatment capacity.
Table 7.1 Preliminary Cost Comparison for 
"Zero Sludge" System Versus Conventional "Sludge" Treatment 
and Versus Weighted Industry Average (36)

<table>
<thead>
<tr>
<th>Plant Description</th>
<th>Circuit Board Job Shop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production:</td>
<td>3,000 sq. ft. board/day</td>
</tr>
<tr>
<td>Process Water Flow:</td>
<td>100,000 gal/day</td>
</tr>
<tr>
<td>2 shifts, 5-day week, 250 operating days/year</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Zero-Sludge Recovery System ($,000)</th>
<th>Convtn. Sludge System ($,000)</th>
<th>Industry Average ($,000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Treatment</td>
<td>1,250</td>
<td>450</td>
<td>425</td>
</tr>
<tr>
<td>Water Demineralization</td>
<td>0</td>
<td>225</td>
<td>225</td>
</tr>
<tr>
<td><strong>Total Installed Cost</strong></td>
<td>1,250</td>
<td>675</td>
<td>650</td>
</tr>
</tbody>
</table>

**Annual Operating Cost**

<table>
<thead>
<tr>
<th>Capital Recovery (@ 8% opportunity cost)</th>
<th>186</th>
<th>101</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance @ 4% TIC</td>
<td>50</td>
<td>27</td>
<td>26</td>
</tr>
<tr>
<td>Labor @ $25/person-year</td>
<td>50</td>
<td>75</td>
<td>85-181</td>
</tr>
<tr>
<td>Chemicals</td>
<td>44</td>
<td>76</td>
<td>60</td>
</tr>
<tr>
<td>Electricity @ $0.05/kw.hr</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Water-in/out @ $3.00/1000 gal</td>
<td>8</td>
<td>75</td>
<td>50-125</td>
</tr>
<tr>
<td>Waste disposal @ $200-400/ton</td>
<td>0</td>
<td>24-48</td>
<td>24-96</td>
</tr>
<tr>
<td>Miscellaneous Costs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manifesting</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Permit costs</td>
<td>0</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Insurance, general liability</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Legal, environmental impairment</td>
<td>0</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td><strong>Total Annual Cost</strong></td>
<td>353</td>
<td>390</td>
<td>342</td>
</tr>
</tbody>
</table>

- 26 -
7.4.2 Assumptions

In this initial comparison the following assumptions were made:

Capital Costs

Equipment Installed Cost

The capital cost of the zero-sludge recovery system is comprised of five treatment systems; acid copper treatment, chelated copper treatment, nickel treatment, tin/lead treatment and a demineralization unit. In addition a distributed process control system is an integral part of the total waste treatment package.

In contrast, the costs for conventional treatment systems are more difficult to quantify. The study carried out by Sandberg (36) illustrates the variability; installed capital costs of conventional treatment systems ranged as follows:

- $20-400,000 for systems treating up to 20,000 gals/day
- $155-477,000 for systems treating up to 50,000 gals/day
- $120-550,000 for systems treating up to 100,000 gals/day.

The one system described for treating 200,000 gals/day had an installed system cost of $112,000. Taking the cost data from Sandberg’s study and weighting the costs from the different installation capacities to give a cost for treating 100,000 gals/day gives an industry average cost of $425,000 which is within 5% of the value estimated by the client for the present case study site in Table 7.1.

While the zero-sludge recovery system contains a demineralization unit, conventional systems do not. Since most printed circuit board plants require de-ionized water for rinsing and for reconstituting baths, the additional capital and operating costs of a demineralization system must be added for conventional systems.

Annual Operating Costs

These comprise the capital cost repayment (cost recovery), maintenance costs, labor costs, electrical utilities and process water/sewer use costs. In addition the cost of offsite waste disposal, mainly comprising heavy metal sludge disposal is included along with some miscellaneous costs.
Cost of Financing

A straight line depreciation over a 10-year lifetime was calculated using an 8% opportunity cost of capital.

Maintenance

Figures for maintenance costs for waste treatment systems vary widely throughout the printed circuit board industry. In many cases the real costs are buried in overall plant maintenance costs. An annual cost of 4% of total installed system cost (TIC) seems typical (36).

Labour

In the comparison of labour costs it has been assumed that the zero-sludge system with its higher degree of process automation would need fewer personnel for operation than a conventional treatment system. The skills level required for the former system, however, would be higher with typically one junior engineer per shift required compared to a supervisor and technician for a conventional treatment system.

Electricity

The electrical utility costs for the zero-sludge technology are higher due to the larger number of pumps and the power requirements of the electrowinning cells.

Process Water

Both plants have been assigned the same charges ($3.00/1,000 gallons) for process water inflow, and outflow to sewer. It is realized that both of these costs will increase in the future although the water discharge costs may see a higher rate of increase as municipalities begin to impose realistic costs for waste treatment.

The cost of process water inflow and outflow to sewage is significant, as illustrated in Table 7.1. The average industry price range of $2.00 to $5.00 per thousand gallons, translates to a cost ranging between $50,000 and $125,000.

For the zero-sludge system it has been assumed that around 90% of process water is recycled; in the case of the conventional system total discharge has been assumed.
Waste Disposal

Based on the industry survey data, this factor was found to be the most variable. It is clearly also the most susceptible to future increases. Costs recorded in the present study ranged from $135-672 per ton while Sandberg's study indicated costs of $52-270 per drum (approximately four 55-gallon drums per ton, giving a range of $200-1,080 per ton). In this study a conservative range of $200-400 per ton was used for cost comparison, but the industry average was assigned a more realistic $200 to 700 per ton.

Cost Recoveries

In the present comparison no credit has been assigned for cost recoveries of recovered metals or process chemicals. These could have a future significance but their magnitude is still small compared to the major cost elements: installed capital cost and the costs of waste disposal and water (in and out).
7.4.3 Conclusions

The data from Table 7.1 indicate that zero-sludge recovery systems are more economical than conventional sludge based systems for medium to large sized printed circuit board plants. While this is still a very preliminary cost comparison, a number of significant conclusions can be drawn:

1. **Overall Cost Comparison:** The major cost differences between the two approaches are:
   - the higher capital cost of the zero-sludge system compared to conventional treatment
   - the large savings in water costs (both for influent water and for discharge to sewer) associated with the zero-sludge system
   - the rapidly escalating costs for the land disposal of toxic wastes in the case of conventional treatment systems.

2. **Break-Even:** The present comparison shows that a cost breakeven situation between the two waste treatment approaches has been reached for certain plant sizes and types of operation in specific geographic locations. If we apply some of the higher rates for offsite waste disposal and water (in and out) observed in the present study, then the zero-sludge recovery system is much more cost effective than conventional treatment.

3. **Sensitivity Analysis** Since the above comparison was only carried out for one moderately large circuit board facility, it is difficult to extrapolate the results to other types and sizes of plants, differing geographic and regulatory situations, and to other heavy metal generating industries. It would be desirable, therefore to carry out a more detailed economic analysis to investigate the sensitivity of the breakeven situation to these other variables.

4. **Capital Cost of Zero-Discharge Systems:** As with any new technology, the current capital costs of zero-sludge systems represent a significant element of engineering design and installation costs. This component should change as systems become more established, with a higher element of pre-assembly and skid mounting incorporated to decrease installation costs.

5. **Economic Models:** In this preliminary comparison, a fairly simplistic approach was adopted. No attempt was
made to examine the possible benefits of capital equipment tax write-offs, the impact of various regulatory incentives such as differential process water/sewer use costs, etc. A more precise calculation of capital depreciation using the capital recovery approach was considered but was not adopted because of the magnitude of the other unknown factors. A more detailed analysis of the costs of waste management of heavy metals, incorporating the role of these factors is needed.

6. **Less Tangible Factors**: It was also difficult to quantify some less tangible costs, such as insurance costs, contingency for legal liability for possible future landfill pollution incidents, and impact of a company's waste management strategy on its corporate public or investor profile. There is a need in California for a study which examines the influence of these important factors.

7. **Size and Type of Plant** One result of the industry survey was the finding that the most appropriate waste management strategy may well vary according to the size and nature of the circuit board plant. A full zero-discharge system involving segregation of all waste streams and separate treatment processes for each stream may well be economically impractical for smaller plants. Selected recovery of major pollution point sources combined with some in-plant changes and conventional treatment of residual waste streams may be the most cost-effective solution for these plants.

8. **Conventional Treatment System Write Off**: Many companies with recently installed conventional treatment systems are now facing the prospect of writing off this investment and moving to a resource recovery system. While this is clearly a burden, landfill restrictions and escalating disposal costs will make it inevitable. For smaller dischargers there is still the possibility of converting existing sludge systems to provide a more recyclable sludge, such as the use of borohydride precipitation and recycling through a metal refiner. Alternatively the use of some post sludge treatment system such as redissolution and electrorecovery of the mixed metals also has considerable attraction. This type of technology, however, is not presently available.
3. **INDUSTRY CASE STUDIES**

3.1. **Case Study Goals**

The main goals of the case study were defined as follows:

1) To examine current waste management practices, performance and costs for three printed circuit board plants varying in size and type of work.

2) To examine the technical and economic feasibility of implementing further waste reduction strategies at each of the case study sites, including the use of resource recovery technologies.

3) To define the immediate waste management options and strategies for each of the sites, in the light of decreasing sludge disposal facilities and increasing environmental pressures both through legislation and enforcement.

3.2. **Case Study Methodology**

The methodology of carrying out the case studies is summarized below:

1) A number of plants were visited to select appropriate study sites. Three sites were selected based on their size, type of operation, and level of interest in cooperating with the survey.

2) Initial data was obtained via the Industry Survey questionnaire to summarize waste management practices, performance and costs.

3) Each of the three case study sites was visited and a member of senior management was interviewed to review and expand the data obtained in the questionnaire.

4) In cooperation with the plant environmental manager each of the facilities was surveyed. First, an evaluation of the printed circuit board production facilities was carried out in order to define the various waste sources. Second, an assessment of the existing waste treatment system was carried out.
5) Schematics covering the main process details of the plating operations and the waste treatment system were prepared for each case study site.

6) Some general discussions were held with environmental and senior management staff at each plant site, to sound out their opinions on current environmental issues, legislation and general enforcement climate. These views, along with comments from other survey sites are reflected in the conclusions to the report.

7) Possible routes and strategies for achieving further waste reduction via the implementation of various levels of resource recovery technology were examined and discussed with the staff at each site.

8) The relevant sections of the case study reports were reviewed with each of the study site managers before drafting the final report.
8.3 Case Study Site A

8.3.1 Site Description

Case Study Site A is a small specialized printed circuit board plant located in the south San Francisco Bay area. The main features of the operation are summarized below:

<table>
<thead>
<tr>
<th>Feature</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Revenue</td>
<td>$2-3 Million</td>
</tr>
<tr>
<td>No. of Employees</td>
<td>50</td>
</tr>
<tr>
<td>Shop Type</td>
<td>Printed Circuit Board Job Shop</td>
</tr>
<tr>
<td>Plated Board Area</td>
<td>Extremely Variable</td>
</tr>
<tr>
<td>Type of Boards</td>
<td>Single/Double Sided, Multilayer, Flexible &amp; Other</td>
</tr>
<tr>
<td>Metals Plated</td>
<td>Copper, Tin, Lead, Nickel, Gold.</td>
</tr>
<tr>
<td>Other Regulated Chemicals</td>
<td>Fluoride</td>
</tr>
<tr>
<td>Daily Water Usage</td>
<td>20,000 gal</td>
</tr>
</tbody>
</table>

8.3.2 Waste Management Operations

Waste Treatment System Summary:

<table>
<thead>
<tr>
<th>Current System</th>
<th>Conventional Sludge Treatment System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost</td>
<td>$50,000</td>
</tr>
<tr>
<td>Date of Installation</td>
<td>Mid-1983</td>
</tr>
</tbody>
</table>

Annual Waste Treatment Statistics:

<table>
<thead>
<tr>
<th>Cost</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (In &amp; Out) Cost</td>
<td>$7,200</td>
</tr>
<tr>
<td>Treatment Chemicals</td>
<td>$9,500</td>
</tr>
<tr>
<td>Sludge Generated</td>
<td>Approx. 4 tons/yr</td>
</tr>
<tr>
<td>Cost of Disposal</td>
<td>Approx. $3000</td>
</tr>
<tr>
<td>Labor</td>
<td>1 Person Year</td>
</tr>
</tbody>
</table>
Manufacturing Processes:

This is a small specialist printed circuit board production facility, targeted mainly at complex prototype and short flexible circuit production runs. The general layout of the plant is shown in Figure 8.1. This shows both production and waste treatment areas. A more detailed schematic of the printed circuit board plating area is shown in Figure 8.2. The plating operation is based entirely on manual production.

The company has already made several process design changes aimed at waste reduction and easing waste management requirements. These changes include:

1. Segregation of waste streams
2. Strict control of rinse water usage
3. Reuse of rinse water, wherever compatible
4. Erection of spill containment barriers
Plant A Layout

Shearing

Air Condit'g

Drilling

N/C Program

Screening

Lobby

Shipping

Lab

Inspect

Test

Waste Treatment

Chemical Storage

Fabric'n Room

Multilayer Assembly & Press

Dry Film

Touch Up

Plating Area

Fig. 8.1
Plant A Plating Area

Fig. 8.2

- Nickel Plate
  - 400 gal

- Tin/Lead Plate
  - 400 gal

- Acid Copper Plate
  - 400 Gal

- Acid Copper Plate
  - 400 Gal

- Floor Sump

- Caustic Peroxide
  - Rinse
  - Alkaline Cleaner
  - Acid Bifluoride
  - Rinse
  - Cleaner
  - Sulphuric Peroxide
  - Rinse
  - Bisulphate Precoat
  - Catalyst
  - Rinse
  - Accelerator (dil Acid)
  - Electroless Copper
  - Copper Drag Out
Waste Treatment System Description

The company assigns a very high priority to waste management; the existing waste treatment system, shown schematically in Figure 8.3, is well maintained and operates efficiently. A general view of the sludge treatment system is shown in Figure 8.4.

The major features of the process are:
1. Segregation into metal-bearing and metal-free solutions and their collection in floor sumps.
2. Ferrous sulfate treatment of chelates.
3. Sodium hydroxide/calcium chloride precipitation
4. Polyelectrolyte coagulation and clarification
5. Bag filtration of the sludge
6. Recombination of the treated solution with the metal-free stream and final discharge pH control.
7. Periodic collection of sludge from bags into drums.
8. Disposal of sludge drums to landfill

The system is reported to work satisfactorily and well within the local discharge limit of 1.4 ppm of Copper. Infrequent discharge excursions have been caused by equipment failure, or operator error (typically accidental spills).

This type of conventional precipitation system is very common for this industry. It relies on the insolubility and ease of filtration of the heavy metal hydroxides. The sludge produced ranges from 5% to 40% of total metal depending on the type of filtration method used.

Apart from the requirement to dispose of sludge, the major limitations of the system are:

1. Sensitivity to unexpected concentrations of various chemicals, for example resulting from a spill, which can either affect the metal (in)solubility or overload the clarifier
2. Problems in handling certain difficult-to-treat materials, such as fluorides, chelates, and cyanides, which require additional treatment
3. Inability to meet future increasingly stringent discharge limits
Fig. 8.3 Plant A Waste Treatment System

Metal Free Solutions

- Sodium Hydroxide
- Ferrous Sulfate
- Polyelectrolyte
- Calcium Chloride
- Sulfuric Acid

Stock Tanks

Metal Bearing Solutions

Collection Sump

Bag Filtration

Clarification & Sludge Separation

Discharge pH Control

Sewer

Landfill Disposal

Drums

Sludge to Drums
Fig. 8.4 Plant A Waste Treatment System

General view of a typical conventional waste treatment system. Treatment – precipitation tanks on upper level. Chemical storage and dosing systems in right foreground. Filter bags of sludge are shown in left foreground.
8.3.3. **Recommendations for Waste Reduction/Resource Recovery**

The management of this plant have already reviewed their waste management options and identified future waste reduction goals. These include:

1. **Replacement of the fluoride containing solder electroplate bath with an organic chelate version, thus eliminating fluoride.** To date this has not been implemented, presumably due to the cost of dumping 500 gallons of valuable process bath.

2. **Maximizing reuse of process water.** This can only be achieved by segregating metal-free, clean streams followed by treatment and return to the process. One problem which could arise is that as process water usage is reduced by more efficient rinsing and a greater degree of recycling, the resulting metal concentration levels in the final effluent may actually increase, since the volumes being discharged are much smaller. Since concentration based standards are based on the volume of discharge they could actually penalize the efficient water user. In this situation, a clear case is demonstrated for the implementation of mass based standards.

3. **Reduction or possible elimination of sludge generation.** In proposing additional options or strategies for further waste reduction via the implementation of resource recovery technologies, the first requirement is that any recommendations must be consistent with the financial and technical resources of the company. Possible resource recovery options for consideration by the plant include:

4. **Segregation and collection of the major acid copper sources (electroplate, etchants, etc.).** Provide a small manual cation ion-exchange system to treat these sources. The amount of metal required to be recovered is less than 1 Kg per day, so that the regenerant from the ion-exchange collection step could easily be treated by a small electro-recovery cell, allowing recovery of copper as metallic sheet. The estimated total capital cost for this option is about $35,000.

5. **Similarly, the chelated copper from the electroless plating operation could be treated directly by a small anion ion-exchange system.** The regenerant could also be recovered by electrowinning. The implementation of this option would eliminate the need for ferrous sulfate addition, used to breakdown and precipitate chelated copper. This process generates large amounts of sludge (from the excess FeII) and represents a major
portion of the total sludge generated. The estimated total capital cost for this option is about $30,000.

6. The minor residual metal streams, mainly tin/lead could then be treated with sodium borohydride. This strong reducing agent generates a dense, pure metallic precipitate which could have the effect (at 90+% metal) of reducing the annual 4 tons of sludge (at 10% metal) to approximately half a ton.

In summary, a total capital investment of $70-90,000 could eliminate up to 90% of this plant's offsite waste disposal costs.
8.4 Case Study Site B

8.4.1 Site Description

Case Study Site B is a small-to-medium size circuit board plant located in the northern San Francisco Bay area. The main features of the site are summarized below:

<table>
<thead>
<tr>
<th>Feature</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Revenue</td>
<td>$2 to $3 million</td>
</tr>
<tr>
<td>No. of Employees</td>
<td>45</td>
</tr>
<tr>
<td>Shop Type</td>
<td>Printed Circuit Board Job Shop</td>
</tr>
<tr>
<td>Plated Board Area</td>
<td>350 sq. ft./day</td>
</tr>
<tr>
<td>Type of Boards</td>
<td>Single/Double Sided, Multilayer</td>
</tr>
<tr>
<td>Metals Plated</td>
<td>Copper, Tin, Lead, Nickel, Gold</td>
</tr>
<tr>
<td>Other Regulated Chemicals</td>
<td>None</td>
</tr>
<tr>
<td>Daily Water Usage</td>
<td>30,000 gal</td>
</tr>
</tbody>
</table>

8.4.2 Waste Management

Waste Treatment System Summary:

- Automatic transferred-bed anion cation ion-exchange system
- 50% reuse of process water
- Ion-exchange regenerant converted to sludge
- Aluminum chip treatment of copper concentrates

Capital Cost: est. $200,000
Date of Installation: pre-1983
### Annual Waste Treatment Statistics:

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (In &amp; Out) Cost</td>
<td>$10,800</td>
</tr>
<tr>
<td>Treatment Chemicals</td>
<td>$32,000</td>
</tr>
<tr>
<td>Sludge Generated</td>
<td>Approx. 6 tons/yr</td>
</tr>
<tr>
<td>Cost of Disposal</td>
<td>Approx $34,560 (all wastes)</td>
</tr>
<tr>
<td>Labor</td>
<td>0.5 Person Year</td>
</tr>
</tbody>
</table>

### Production Facility:

Site B is significantly larger in size than Site A. It is a conventional printed circuit board shop targeted mainly at small-to-medium sized production runs. A schematic of the plating area layout is shown in Figure 8.5.

### Waste Treatment System Description:

The waste treatment system in place at this site is quite complex. The system, which is shown schematically in Figure 8.6, is based on segregation of waste streams and treatment as follows:

1. **Metal bearing rinse solutions:** The metal bearing solutions, (approx 50% of the daily water usage) are collected and passed through a Transferred Bed cation/anion ion-exchange system which removes the heavy metals and their salts. The resulting deionized water is returned to the plant for reuse in rinses and chemical make up. The resin is regenerated after pneumatically transferring it to a separate column. The metals are obtained as a sludge which is filtered in a filter-press and drummed.

2. **Copper drag-out and other copper concentrates:** After electroplating, the printed circuit boards are rinsed in static water tanks (drag-out tanks) before the running rinses. These are allowed to build up to 25%-50% of the plating bath concentration and then collected and replaced with fresh water. This concentrated solution is combined with bath dumps and treated with scrap aluminum chips. This precipitates the copper and aluminum hydroxide which is separated and drummed. The use of this drag-out process is estimated to reduce the copper loading on the treatment system by as much as 50%.
Plant B Waste Treatment

Fig. 8.6

- Sulfuric/Peroxide Spent Etch Solution
- Solution for Reuse
- Copper Drag Out Solutions
- Contaminated Rinse Solutions
- Metal Free Rinse Solutions
- Regen Solutions
- Caustic
- Filter Press
- Sludge
- Drum
- Metall Copper Aluminum Sulphate
- Metal Copper Aluminum Sulphate
- Copper Concentrate Precipitation
- D.I. Water
- Return to Rinses
- Transferred Red Ion Exchange
- Cation Exchange
- Anion Exchange
- Crystalline Copper Sulphate
- Drum
- Chiller
- Etch Recovery
- Scrap Aluminum Metal
3. Spent etch solutions: Site B employs a sulfuric acid/peroxide etch process. In this process, the etching power of the hot solution is maintained by periodic additions of Hydrogen Peroxide. The copper which builds up in solution is periodically removed by chilling. The cooling process causes precipitation of copper sulfate, which is removed from the chiller by an auger and drummed. The copper sulfate produced is generally sufficiently pure for resale.

4. Metal-free solutions: Approximately 50% of the process water usage is free from heavy metals and can be combined with the regenerant streams before being directly discharged.

This facility demonstrates a high degree of process water reuse, but is still dependent on landfill disposal of sludge. The main potential problem area is the reliance on drag-out tanks. The requirement for periodic, manual replacement of the drag-out solutions presents a potential problem; if allowed to build up excessively they could overload the treatment system.

A general view of the treatment system is shown in Figure 8.7.

8.4.3. Recommendations for Waste Reduction/Resource Recovery

Several strategies for achieving further waste reduction are available at this facility. Some of these include the option of using resource recovery technologies:

1. Conversion of existing drag-out tanks to spray rinses. The resulting low volume, high concentration waste stream could then be treated by adsorption onto aluminum, as is currently in operation. The capital cost of this modification is $5-10,000. Alternatively, a recovery system outlined below could be adopted.

2. Replacement of the aluminum treatment process for the drag-out rinses with a simple electro-recovery system. This would convert the copper to metal sheets, which could be resold or added to scrap. The manual exchange of the solutions would be replaced by a spray rinse, combined collection system. The estimated capital cost of this option is $20-25,000.

3. Replacement of the sludge precipitation of the regenerant concentrates by an electro-recovery system. The recovered metals could be resold or disposed of as scrap. Capital cost of this option: $20-25,000

In summary, a capital investment in the range $60-100,000 would be required to upgrade this facility's current waste management system and eliminate 80-90% of the current offsite sludge disposal requirements.
Fig. 8.7  Plant B Waste Treatment System

Control panel and moving–bed ion exchange system in foreground. Storage and treatment tanks in background. Sludge filter–press on right.
8.5. **Case Study Site C**

8.5.1 Site Description

Case Study Site C is a major printed circuit board plant located in Orange County. The relevant operating data are summarized below:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Revenue</td>
<td>$20 to $25 million</td>
</tr>
<tr>
<td>No. of Employees</td>
<td>160</td>
</tr>
<tr>
<td>Shop Type</td>
<td>Printed Circuit Board Job Shop</td>
</tr>
<tr>
<td>Plated Board Area</td>
<td>5,400 sq. ft./day</td>
</tr>
<tr>
<td>Type of Boards</td>
<td>Multilayer Only</td>
</tr>
<tr>
<td>Metals Plated</td>
<td>Copper, Tin, Lead, Nickel, Gold</td>
</tr>
<tr>
<td>Other Regulated Chemicals</td>
<td>Fluoride</td>
</tr>
<tr>
<td>Daily Water Usage</td>
<td>240,000 gal</td>
</tr>
</tbody>
</table>

8.5.2. Waste Management

**Waste Treatment System Summary:**

<table>
<thead>
<tr>
<th>Current System</th>
<th>1) Electrochemical recovery from spray-rinse copper concentrates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2) Similar treatment of tin/lead concentrates</td>
</tr>
<tr>
<td></td>
<td>3) Sludge treatment of residual dilute rinse streams</td>
</tr>
</tbody>
</table>

Capital Cost: $350,000

Date of Installation: 3-5 years old
Annual Waste Treatment Statistics:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (In &amp; Out) Cost</td>
<td>$50,000</td>
</tr>
<tr>
<td>Treatment Chemicals</td>
<td>$36,000</td>
</tr>
<tr>
<td>Sludge Generated</td>
<td>18 tons</td>
</tr>
<tr>
<td>Cost of Disposal</td>
<td>Approx. $20,000/yr</td>
</tr>
<tr>
<td>Labor</td>
<td>2 Person Year</td>
</tr>
</tbody>
</table>

Production Facility:

This site is one of the larger facilities in California and is located in the Los Angeles area. It is again a printed circuit board job shop, but concentrates its market solely on the higher value multilayer boards. As is typical in California, environmental management is a high profile concern with management.

While the current production facility is manually operated, the company is expanding to a nearby site where the manufacturing processes will be fully automatic. A schematic of the current layout of the plating area is shown in Figure 8.8.

Waste Treatment System Description:

The waste treatment system layout is shown schematically in Figure 8.9. In contrast to the two previous study sites, this system is designed with the aim of achieving metal recovery and reduction in process water usage but with no water reuse.

In the production area, water use has been minimized by the use of spray rinses for the first rinse after plating. The waste streams are treated as follows:

1. Concentrated copper rinses: The copper concentrates and comparatively small-volume spray rinse solutions are collected and treated by a high performance (Carbon Fiber Cathode) electrolytic recovery system. This reduces the copper level to ppm levels at which point the streams are combined with the other sources and discharged. In a separate recovery cell the copper metal is simultaneously dissolved out of the carbon fiber and electroplated onto stainless steel starter sheets. The copper metal foil is then peeled off the steel starter sheets and recycled as scrap.

2. Concentrated tin/lead rinses - The tin/lead solutions are treated in a similar but smaller scale electro-recovery process.
3. Other rinses - All the other rinses are combined and treated in a conventional hydroxide precipitation system.

The electro-recovery system, shown in Fig. 8.10, is estimated to recover approximately 10% of the metals. The system performs consistently within the discharge limits except for infrequent excursions generally caused by operator error (spills), which can, in some instances, overwhelm the sludge system.

8.5.3. Recommendations for Waste Reduction/Recovery

There are two main areas where this facility could improve its waste management operations; reduction or possible elimination of its current sludge generation and increased reuse of its process water.

1. Reduction or elimination of sludge: Currently, this facility generates approximately 180 tons of sludge per year, which they are transporting to a mining site metal reclaimer at an annual cost of $20,000. If this sludge were to be transported to landfill, disposal costs could be as high as $200,000. The goal of successive reduction of sludge generation could be achieved by segregation of waste streams into acid copper, chelated copper and tin/lead. Implementation of ion-exchange, electrolytic recovery systems on the acid copper and chelated copper lines. Alternatively, the existing electrolytic recovery systems could be used for ion-exchange regeneration provided that there is sufficient spare capacity. Capital costs of the acid copper recovery system would be in the range $100,000 to $150,000 and the chelated copper system, $80,000 to $100,000.

2. Treatment of the residual tin/lead streams (approximately 15% of total metal could be achieved by utilizing the Venmet, borohydride reduction process to produce a pure metal, salable sludge. The additional capital cost of the Venmet process to treat the volumes involved is estimated at $25,000.

3. Alternatively an ion-exchange/electrolytic recovery system could be used to treat this stream. Estimated capital cost $100,000.

4. Water Reuse: The next obvious step for this facility would be to provide for water reuse. This could be achieved after the precipitation system by either an anion/cation ion exchange system, ultra filtration system or reverse osmosis system.
Fig. 8.10  Plant C Waste Treatment System

Electrolytic Recovery System. Cell/tank assembly on left and control system/power supply on the right.
5. Increased Reuse of Process Water: Implementation of a mixed bed ion-exchange system or alternative demineralization unit would allow a major portion of the process water to be recycled. An estimate of the capital cost for this equipment is $200,000.

In summary, this company, like many others, is facing the possibility of drastically increased water costs and restriction of landfill disposal options. It is currently spending approximately $240,000 per year on waste management of which total water costs are $50,000 and offsite disposal costs $24,000.

An estimate of the capital equipment costs to provide a resource recovery system capturing 85% of total metals and recycling over 90% of process water ranges from $400,000 to $550,000. These costs exclude engineering costs, in-plant changes and installation costs.
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Integrated Waste Management Systems- Case Studies


Application to Other Industries
