GLOSSARY OF TERMS

Terms	Meaning
Acquis Communautaire or *Acquis*	The 'Body of Law' of the European Union covering all legislation prepared and adopted by EU institutions.
ADR	European Agreement for international transport of hazardous substances (Accord Européen Relatif au Transport International des Marchandises Dangerouses par Route)
BAT	Best Available Techniques
BG	Bulgaria
CAP	Common Agricultural Policy
CAS	Country Assistance Strategy
CBC	Cross-border Co-operation
CEE	Central and Eastern European countries
CPC	Clean Production Centre
DDBRA	Danube Delta Biodiversity Reserve Authority or
DfID	Department for International Development
DISAE	Development of Implementation Strategies for Approximation in Environment
EBRD	European Bank for Reconstruction and Development
EDC	Ethylene Dichloride
EEC	European Economic Communities
EIA	Environmental impact assessment
EIB	European Investment Bank
EIS	Environmental impact statement
EIU	Economist Intelligence Unit
EMAS	Eco-management and Audit Scheme
EPI	Environmental Protection Inspectorate
EPR	Environmental Performance Report Ref: 28.
EQS	Environment Quality Standard
ERM	Environmental Resources Management
EWC	European Waste Catalogue
EU	The European Union
GD	Government Decision
GEF	Global Environment Fund
GEO	Government Emergency Ordinance
GMP	Genetically modified products
GO	Government Ordinance
HCl	Hydrogen Chloride
HU	Hungary
HWL	Hazardous Waste List
ICIM	National Institute for Environment Protection
IFI	International Financing Institution
IHW	Industrial Hazardous Waste
IMF	International Monetary Fund
IPH	Institute of Public Health
IPPC	Integrated Pollution Prevention Control
ISPA	EU Instrument for Structural Policies for Pre-Accession (See Section 11.2.4)
IWL	Integrated Waste List
JICA	Japan International Cooperation Agency
LCP	Large Combustion Plants
LEAP	Local Environmental Action Plans
Meuro	Million euro
MoAFF	Ministry of Agriculture, Food and Forests
MHF or MoHF	Ministry of Health and Family
MIR	Ministry of Industry and Resources
MO	Ministerial Order
MP	Member of Parliament
MSW	Municipal Solid Waste

Terms	**Meaning**
MWEP or MoWEP	Ministry of Water and Environmental Protection
MWFEP	Ministry of Water, Forestry and Environmental Protection (former name of MWEP)
NCPC	National Cleaner Production Centre
NEAP	National Environmental Action Plan
NEHAP	National Environmental Health Action Plan
NES	National Environmental Strategy
NIS	National Institute of Statistics
NPAA	National Programme for the Adoption of the Acquis
PCB	Polychlorinated biphenyls
PCT	Polychlorinated triphenyls
PCV	Polyvinyl Chloride
PHARE	EU programme for Polish-Hungarian Assistance for Restructuring, now extended to other Central and Eastern European countries (Section 11.2.1).
PPC	Project Preparation Committee or Pollution Prevention Centre
REC	Regional Environment Centre
REReP	Regional Environmental Reconstruction Programme for SEE countries.
RO or ROM	Romania
ROL	Romanian Lei (for exchange rate, see USD).
SA	Society by Actions (a type of legal entity in Romania)
SAPARD	EU Special Accession Programme for Agriculture and Rural Development (See Section 11.2.5)
SOF	The State Ownership Fund now called APAPS.
SoS	Secretary of State
SR	Romanian Standards
SRL	A Romanian registered company
ToR	Terms of Reference
UNDP	United Nations Development Programme
UNIDO	United Nations Industrial Development Organization
USAID	US International Aid Agency
USD	US Dollar. 1 USD = 30930.0 Romanian Lei (source: Financial Times, 24/10/2001).
VCM	Vinyl Chloride Monomer
WB	The World Bank
WEC	World Environment Centre
WMIS	Wast Management Information System
WWTP	Waste Water Treatment Plant

Final Reports

Volume 1	Main Report: Strategy and Action Plan for Hazardous Waste Management in Romania
Volume 2	Supporting Report 1: Supporting Information for the Strategy and Action Plan
Volume 3	Supporting Report 2: Results of Surveys Conducted
Volume 4	Supporting Report 3: Results of Pilot Projects Implemented
Volume 5	Summary
Volume 6	Pilot Project 1 Promotion of Heavy Metal Recycling Using Existing Smelting Facility
Volume 7	Pilot Project 2 Waste Minimization and Treatment in Metal Surface Treatment Process
Volume 8A	Pilot Project 3A Organic Solvent Reduction
Volume 8B	Pilot Project 3B Responsible Care
Volume 9	Pilot Project 4 Strengthening EPI and Company Capacity in Hazardous Waste Management

INTRODUCTION

As part of JICA Study on Hazardous Waste Management Study for Romania, JICA has conducted 4 pilot projects, of which Pilot Project 2 focused on Waste Minimisation and Treatment in Metal Surface Treatment Processes. Results of all the 4 Pilot Projects including Pilot Project 2 are shown in Final Report Volume 4.

Final Report Volume 7 contains "Best Practice Manual for Waste Minimisation and Treatment in Metal Surface Treatment Processes". JICA has prepared this manual as part of Pilot Project 2 activities.

Best Practice Manual was prepared for use by metal finishers, raw materials suppliers, treatment plant designers, consultants, inspectors, NGOs and other stakeholders to promote and facilitate application of best practice. This document includes technical "case study" examples from the work undertaken in the two pilot project enterprises to illustrate best practice.

BEST PRACTICE MANUAL

for

WASTE MINIMISATION AND TREATMENT
IN METAL SURFACE TREATMENT PROCESSES

(This manual was prepared as part of activities of Pilot Project 2)

This manual was prepared for the JICA Project

Study on Master Plan for Hazardous Waste Management in Romania

⇒ by

National Research and Development Institute for Environmental Protection

– ICIM Bucharest –

Splaiul Independentei 294, Bucharest

⇒ with support and assistance from

Direct Auto Rom Pitesti
Timpuri Noi Bucharest
Environmental Protection Inspectorate Pitesti
Environmental Protection Inspectorate Bucharest
CAST SA Bucharest
MANZ GALVANO-TEC Bucharest
CDM GALVAN (MacDermid) Bucharest

Best Practice Manual
for
Waste Minimisation and Treatment in Metal Surface Treatment Processes

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Chapter 1

Introduction

1 INTRODUCTION

The purpose of this good practice guide is to promote cleaner production and best waste management practice in Romanian metal plating companies. The guide aims to raise awareness of best practice for all those with a role to play in promoting best practice. This includes:

- Enterprise operators, supervisors and managers
- Plating chemical suppliers
- Consultants, designers and specifiers of plating processing plant
- Consultants, designers and specifiers of plating, wastewater and sludge treatment plants
- Pollution inspectors and authorities issuing operating permits for plating enterprises.

This guidance was produced as a result of pilot projects at two Romanian Plating Companies, Timpuri Noi Bucuresti and Direct Auto Rom Pitesti. Best practice for the two pilot enterprises was developed by a working group which included all stakeholders and representatives from the guidance note target audience.

The guidance note demonstrates that pollution prevention pays not just in reducing the environmental impact of plating enterprises but in providing benefits to the enterprise. These benefits include reducing operating costs, improving product quality, improving production throughput, improving the working conditions for operatives and achieving compliance with legislation and obtaining operating permits.

Guidance is provided on how to:

- Reduce water use and wastewater discharges and potential benefits
- Reduce chemical use in plating processes and potential benefits
- Reduce energy use at plating processes and potential benefits
- Treat wastewater from zinc plating processes
- Treat and dispose of sludge from plating WWTPs
- Reduce WWTP capital and operating costs.

The guidance note includes practical examples results and photographs from the implementation work at the pilot enterprises.

1.1 Wastes Generated by the Plating Industry

Wastes generated by plating processes are classified as hazardous waste and include oily wastewaters from degreasing, spent plating and pickling solutions and wastewater containing heavy metals, cyanides, hexavalent chromium, acids, alkalis and organic chlorinated solvent wastes.

Treatment of spent solutions and wastewaters by plating enterprises generates sludges which are classified as hazardous wastes.

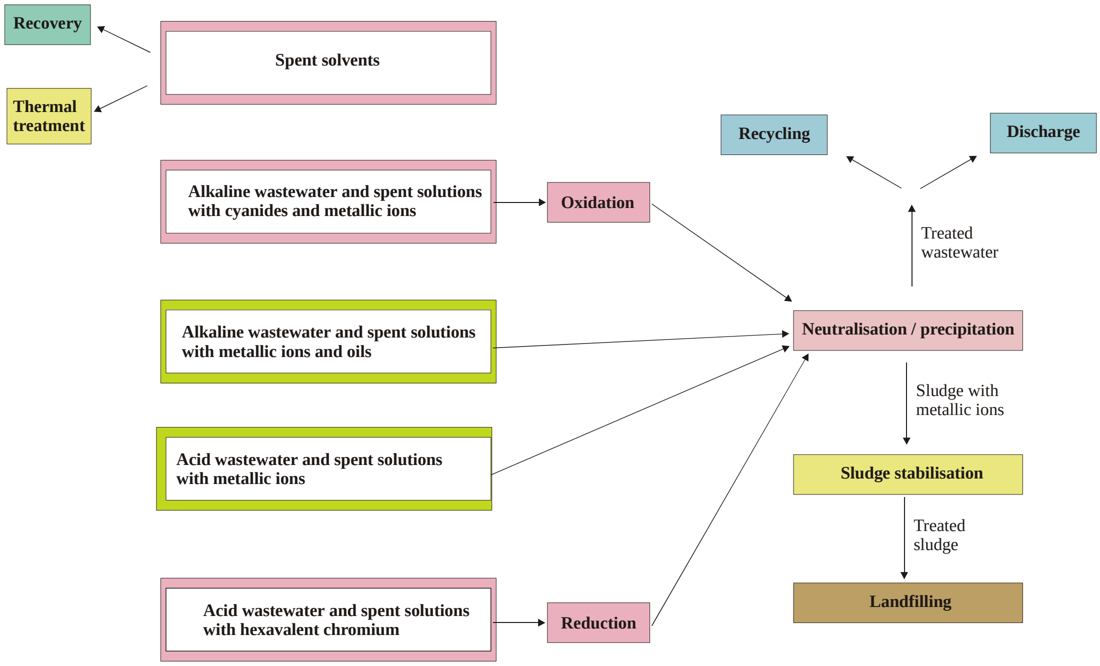


Figure 1.1 Main Types of Wastes Generated from Plating Processes

At the Pilot enterprises cyanide zinc plating solutions where replaced with non cyanide zinc plating solutions and chlorinated solvents used for degreasing where replaced with alkali cleaning solutions. Wastes generated at the pilot enterprises include only acid and alkaline wastewater and spent solutions.

1.2 Waste Management

The waste management hierarchy (Figure 1.2) is a fundamental concept in waste management where preference is given to management techniques further up the hierarchy. Accordingly, a lot of effort is focused on the avoidance of waste generation and minimisation of waste generation (both quantities and hazard).

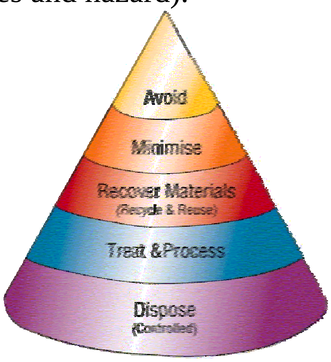


Figure 1.2 Waste Management Hierarchy

Having avoided and minimised as far as practicable, remaining wastes should preferably be reutilised, recycled or subject to material recovery. When considering practicability, economic issues should be taken into account (The principle of Best Available Technique Not Entailing Excessive Cost – “BATNEEC”).

Recovery of metals from spent plating solutions and even waste waters MAY be viable and cost effective, for example for precious metal plating processes and sometimes for copper or cadmium plating.

For wastes / wastewaters the recovery or recycling of which is not practicable, then environmentally sound treatment and disposal must be implemented. Wastes with any hazardous characteristics should be treated prior to disposal.

Ways to reduce, recover, treat and dispose of the wastes generated are provided in this guidance.

Waste minimisation and cleaner production is achieved through ‘People’, ’Systems’ and ‘Technology’. This is recognized and embedded in environmental management system standards for example in ISO 14000, and legislation for example EU IPPC legislation.

People driven opportunities are associated with improvements in operating practices and cost nothing to implement. Good operating practice starts with basic housekeeping and the recognition of opportunities to avoid spillage, breakage, leaks, and loss of time expired materials through faulty ordering and storage practices. The benefits from these opportunities are reaped from training and the promotion of awareness, involvement and ownership of the problems/costs and solutions.

Systems driven opportunities are based on the concept that ‘if you don’t measure you don’t manage’ Production management information systems enable early identification of variance and wastage due to faulty materials, machine malfunction, or poor operator control. System driven opportunities cost very little to implement. The data from systems will support decisions associated with materials specification changes and investments in new technology plant and equipment.

Technology Driven Opportunities are based on changes to plant and equipment to make processes more efficient. Opportunities in this area usually involve capital investment necessitating detailed evaluation and justification. Accurate evaluation can often only be achieved by eliminating aspects of poor efficiency associated with wastes from poor housekeeping and production management.

1.3 Drivers and Barriers to Waste Minimisation

Discussions with enterprises and other stakeholders identified the following drivers and barriers to waste minimisation and cleaner production.

Barriers

- Lack of investment funds;
- Concern over impact on products quality;
- Limited understanding and awareness of technical and process issues;

- Lack of time for system analysis and implementation of improvement measures;
- A general attitude "it works all right as it is".

Drivers

Some minimisation procedures are not costly, but they have a lot of advantages::

- Costs decreasing, so profit increasing;
- Improvement of working conditions;
- Conditions for compliance with legal norms for environmental protection (for example EU IPPC Directive);
- Assist progress towards accreditation according to ISO 9000 and ISO 14000;
- A better image of the company (especially for customers).

Chapter 2

Reducing Water Use and Wastewater Discharge

2 REDUCING WATER USE AND WASTEWATER DISCHARGE

Most of the water used and wastewater discharged from plating processes is associated with rinsing. Effective rinsing is essential to achieve good quality products. Many plating enterprises use low cost water extracted from their own boreholes and charges for disposal of their wastewaters are low. As consequence electroplating enterprises use large quantities of water.

Also wastewater treatment plants at many enterprises have deteriorated beyond repair and the practice of diluting wastewaters with excessive rinse water flows, to comply with discharge standards has become common practice in Romania. This dilution practice is wasteful of natural recourses, distributes hazardous heavy metals into the environment unnecessarily and can have a detrimental effect on the performance of municipal wastewater treatment plants many of which are already overloaded.

Also new companies even small companies are unable to obtain connections to sewer for disposal of there wastewater because the sewer infrastructure is often in need of development and many existing systems are already overloaded. Minimising wastewater is essential for these companies who have to tanker their wastewater off site.

As Romanian legislation aligns with EU Integrated Pollution Prevention and control legislation the pressures on industry to reduce water use and wastewater discharges will increase.

Enterprises utilizing this guidance to address these pressures will benefit from reduced size capital and running cost of effluent treatment plants and reduced operating costs of processes.

Rinse Water Use

To demonstrate the water savings potential we can use the zinc plating activities at the pilot enterprises as an example. A typical zinc plating would line would be as outlined below and in the case of the pilot enterprises would have single stage rinsing.

A conventional zinc plating line consists in:

- Degreasing;
- Rinsing after degreasing (only after chemical and anodic degreasing);
- Pickling;
- Rinsing after pickling;
- Zinc plating;
- Rinsing after zinc plating;
- Activation;
- Passivation;
- Rinsing after passivation.

The Electroplating Chemical Suppliers Association recommend rinse water dilution ratios after each main stage of the technological flow in order to comply with the quality requirements these are shown in Table 2.1

Table 2.1 Recommended Dilution Rinse Ratios

Stage	*Dilution ratio*
Rinse after chemical degreasing	500
Rinse after pickling	1000
Rinse after zinc-plating	2000
Rinse after passivation	2000

The optimum number of the counter-current rinse stages is established with consideration to disposal route of treated waste water, cost of additional tanks, water saving benefits, and space available to accommodate additional tanks.

Water use and water savings potential is calculated using the formula below:

$$\textbf{Rinse Water Flow-rate (l/h) = carry-over (l/h) x dilution ratio}^{1/n}$$

where: n – number of counter-current rinse stages
dilution ratio – according to Table 2.1

Based on the formula above, necessary rinse water flow-rates are estimated, for different values of the carry-over and taking into account the number of rinse stages – Table 2.2(a,b,c,d)

Table 2.2 (a) Necessary Rinse Water Flow-Rates After Chemical Degreasing

Carry-over (l/h)	***Rinse water flow-rate (l/h)***			
	1 rinse stage	2 rinse stages	3 rinse stages	4 rinse stages
0.5	250	11	4	2
1	500	22	8	5
1.5	750	34	12	7
2	1000	45	16	9
2.5	1250	56	20	12
3	1500	67	24	14
3.5	1750	78	28	17
4	2000	89	32	19
4.5	2250	101	36	21
5	2500	112	40	24

Table 2.2 (b) Necessary Rinse Water Flow-Rates After Pickling

Carry-over (l/h)	*Rinse water flow-rate (l/h)*			
	1 rinse stage	2 rinse stages	3 rinse stages	4 rinse stages
0.5	500	16	5	3
1	1000	32	10	6
1.5	1500	47	15	8
2	2000	63	20	11
2.5	2500	79	25	14
3	3000	95	30	17
3.5	3500	111	35	20
4	4000	126	40	22
4.5	4500	142	45	25
5	5000	158	50	28

Table 2.2 (c) Necessary Rinse Water Flow-Rates After Zinc Plating

Carry-over (l/h)	*Rinse water flow-rate (l/h)*			
	1 rinse stage	2 rinse stages	3 rinse stages	4 rinse stages
0.5	1000	22	6	3
1	2000	45	13	7
1.5	3000	67	19	10
2	4000	89	25	13
2.5	5000	112	31	17
3	6000	134	38	20
3.5	7000	157	44	23
4	8000	179	50	27
4.5	9000	201	57	30
5	10000	224	63	33

Table 2.2 (d) Necessary Rinse Water Flow-Rates After Passivation

Carry-over (l/h)	*Rinse water flow-rate (l/h)*			
	1 rinse stage	2 rinse stages	3 rinse stages	4 rinse stages
0.5	1000	22	6	3
1	2000	45	13	7
1.5	3000	67	19	10
2	4000	89	25	13
2.5	5000	112	31	17
3	6000	134	38	20
3.5	7000	157	44	23
4	8000	179	50	27
4.5	9000	201	57	30
5	10000	224	63	33

The data in Table 2.2 shows that for a conventional zinc plating line, with 1 rinse stage after each technological operation and for a carry-over of 1 l/h, the water flow-rate is 5500 l/h.

The plating lines installed at the pilot enterprises have been installed with multiple rinse stages (Table 2.3, Figure 2.1) and reduced water flow rates to 80 litres /hour at TN and 58 litres /hour at DAR for a 1 litre /hour carryover.

Table 2.3 Stages of Technological Flow

Rinse after	***Number of counter-current rinse stages***	
	Timpuri Noi (acid Zn plating)	Direct Auto Rom (alkaline Zn plating)
Degreasing	2	2
Pickling	3	2
Zinc plating	2	3
Passivation	3	3

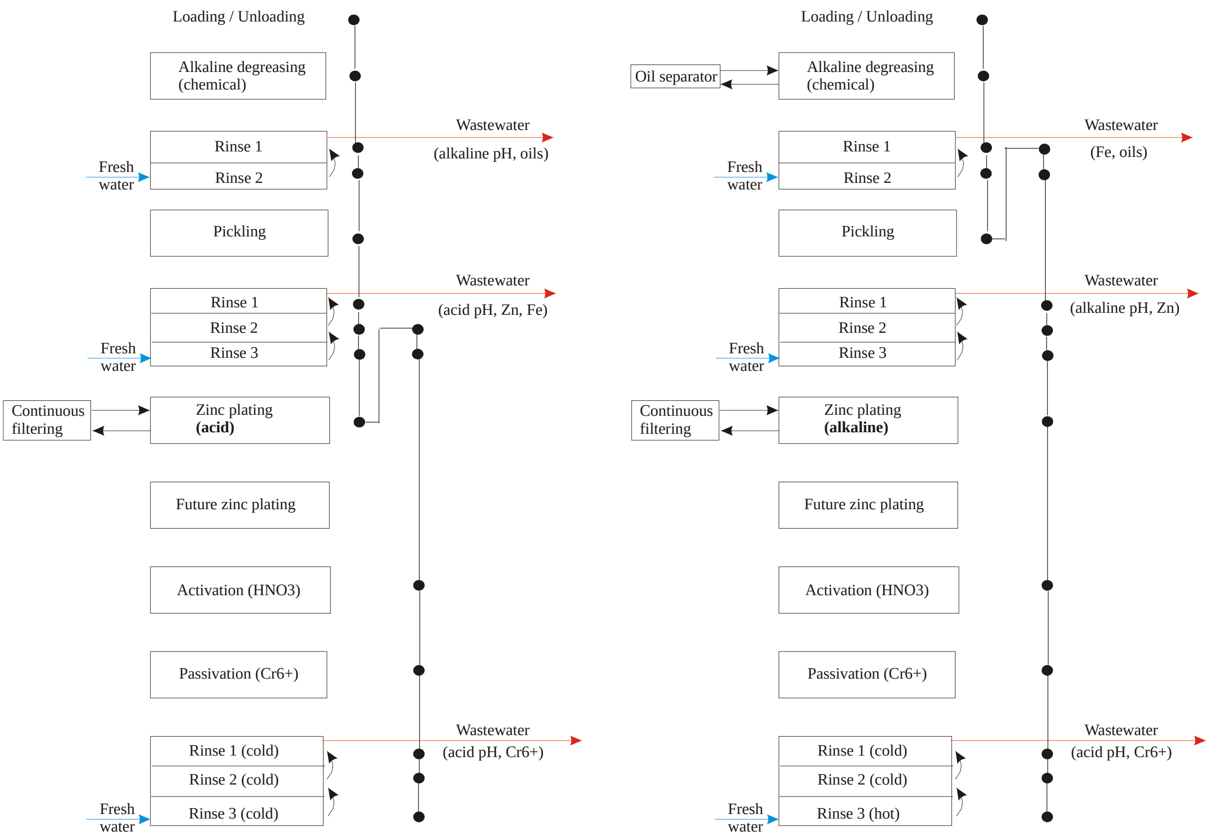


Figure 2.1 Zinc Plating Technological Flow

Note each pipe supplying water to rinse stages must be equipped with a simple flow-meter in order to allow the flow-rate adjustment according to specific conditions (number of barrels or / and racks per hour, carry-over etc.)

RESULTS

Conventional Process Single stage rinsing	5500 litres /hour
TN Process Multistage Countercurrent Rinsing	80 litres /hour
DAR Process Multistage Countercurrent Rinsing	58 litres /hour

Best practice procedures for water consumption minimisation

- ***Establish water flow-rates using formula and rinse ratios recommended by electroplating chemical suppliers association***
- ***Adjust and monitor water flow-rates to obtain recommended dilution ratios***
- ***Supplying water only during working hours***

International studies [2] have developed performance standards for hydrochloric acid consumption at pickling processes (Figure 2.2), companies can benchmark their performance using this information.

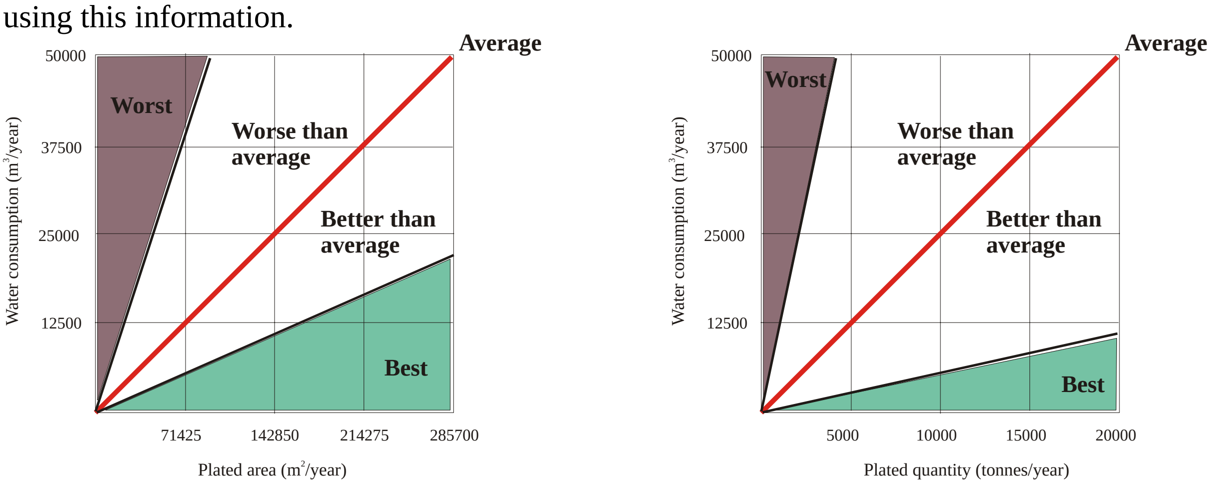


Figure 2.2 Water Use Benchmarks for Metal Finishing Industry

RESULTS

BEST = up to 0.07 m^3 water / m^2 of plated surface

Average water consumption for the two companies has been:

Timpuri Noi – 0.07 m^3 / m^2
Direct Auto Rom – 0.02 m^3 / m^2

Chapter 3

Reducing Chemical Use at Plating Processes

3 REDUCING CHEMICAL USE AT PLATING PROCESSES

The pilot project working group considers that the quality of plating solutions manufactured in Romania although lower cost is not as good as imported plating solutions. This results in greater quantities of plating solution use and greater quantities of spent plating solutions for disposal.

It is estimated that in Romania plating solution costs account for between 20 -25 % of plating costs. Reducing the use of chemicals will contribute considerably to the plating enterprise profit and to improving the environmental impact of the enterprise

The cost saving benefits from reducing chemical use is associated with, reducing raw materials consumption, lower quantities of spent solutions for treatment and disposal.

Reduction in the use of plating chemical solutions is achieved mainly through improving production management and operating practices.

Management and operating practices to reduce chemical use include improving:

- Reducing carryover (including component racking arrangements)
- Chemical purchase, storage and stock rotation
- Monitoring and control of bath chemicals
- Prolonging the life of bath chemicals

Reducing Carry-over

Quantities of carry-over widely vary depending on the shape of the pieces, dripping-time, bath temperature (which influences the viscosity).

Carry-over of technological solutions has bad influence on the technological flow (that is also reflected into costs), such as:

- Contamination of the baths down-stream the technological flow (and changing their characteristics, reducing their lifetime);
- Loss of chemical substances, hence increase consumption of raw materials;
- Increase necessary water volumes in order to achieve the recommended rinse ratios;
- Increase content of chemicals in wastewater, hence larger costs for wastewater treatment;
- Larger quantities of sludge.

Although the carry-over can not be totally removed, the quantities can be reduced by simple, no-cost procedures.

Best practice procedures for carry-over minimisation

➢ ***Increase dripping-time***

- increase dripping-time allows the solution to drain from the pieces
- professional associations recommend a dripping-time of minimum 20 secs
- studies showed that increase of dripping-time from 15 to 30 secs leads to a 50 % increase of recovered electrolyte

➢ ***Slow withdrawing of pieces***

- allows the solution to drain from pieces more efficient than in the case of rapid withdrawing

➢ ***Reducing entrapment***

- depends on the shape of pieces and can be reduced by changing the way of positioning pieces on racks

Installing drip boards

- drip boards are installed between tanks and are positioned in such a way to allow the solution to come back into the source tank

➢ ***Installing drip tank***

- is useful in case of automatic lines, where one load can be left dripping, while transporters are moving other racks
- collected solution is discharged back to source tank

Improve Purchase and Storage Practices

Chemical substances purchased can be used immediately or be stored for use later . Storing large quantities of raw materials has the risk of them exceeding their shelf life and a need to dispose of them. Correct planning of purchases and a good control of stocks must be practiced.

Best practice procedures for purchase and storage system

- ***Purchase quantities that are appropriate to the process needs***
- ***Store containers in appropriate conditions and label to show clearly date of purchase and expiry date***
- ***Keep a clear register of raw materials stocks, in order to use the oldest first***

Monitoring and Control of Plating Bath Chemical Solutions

Proper control of chemical conditions of process baths can reduce chemical use. Chemicals are used to, top up existing baths, replace spent baths and correct active substance concentrations in baths.

In many cases the addition of chemicals to baths and the replacement of bath chemicals is not based on the condition of the solutions which is wasteful of chemicals.

.

Best practice procedures for technological parameters control

- ***Check operating conditions and maintain a tight control on chemicals adding***
- ***Use proper measuring equipment that incorporating automatic adjustment***
- ***Check Performance at regular time intervals or after a certain production quantities (barrels, racks, plated surface) and add chemicals according to the results***

- in case of lines with large output is useful to use an automatic system for measuring and chemicals addition

Table 3.1 presents the main types of analysis needed for solution maintenance within the zinc plating technological flow.

Table 3.1 Analysis for Solution Maintenance

Bath	***Type of technological solution***	***Type of analysis***	***Reagents and laboratory equipment***
Alkaline degreasing	Alkaline	Alkalinity	hydrochloric acid (known normality) phenolphthalein (indicator) distilled water laboratory glassware
Pickling	HCl	Acidity	sodium hydroxide (known normality) methyl orange (indicator) distilled water laboratory glassware
Alkaline zinc plating	Alkaline	Zinc	EDTA (known normality) buffer solution black eriochrome T (indicator) distilled water laboratory glassware
		NaOH	sulphuric acid (known normality) indicator distilled water laboratory glassware
Acid zinc plating	Acid	Zinc	EDTA (known normality) buffer solution black eriochrome T (indicator) distilled water laboratory glassware
		Chloride	potassium bichromate silver nitrate (known normality) sodium acetate distilled water laboratory glassware
		Boric acid	sulphuric acid (known normality) sodium hydroxide (known normality) methyl red (indicator) distilled water laboratory glassware
Activation	HNO_3	pH	pH-meter for laboratory use laboratory glassware
Passivation	Passivation agent (with CrO_3)	pH	pH-meter for laboratory use laboratory glassware

Prolonging Lifetime of Technological Solutions

Lifetime of technological solutions is diminished by accumulation of non-active substances or sediments in tanks. This is most evident in degreasing and pickling baths.

<u>Best practice procedures for prolonging lifetime of technological solutions</u>

- ***Analysing and implementing all possible measures to reduce contamination from the surface of the pieces before the cleaning stages (degreasing, pickling)***
- ***Proper use, at designed parameters, of continuous filtering equipment and of cooling equipment for zinc plating solution***

International studies [3] have developed performance standards for hydrochloric acid consumption at pickling processes (Figure 3.), companies can benchmark their performance using this information.

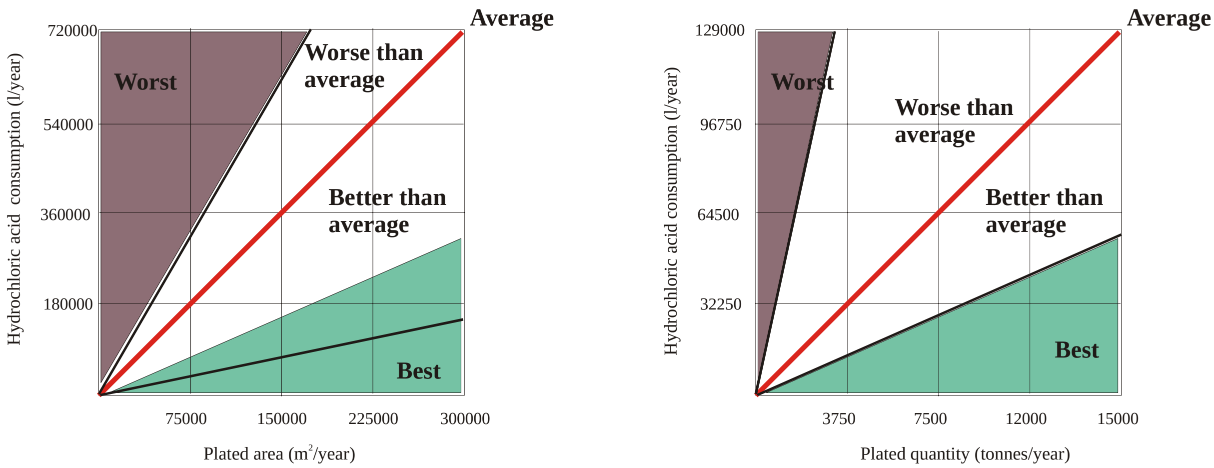


Figure 3.1 Acid Use for Pickling Benchmarks for Metal Finishing Industry

RESULTS

BEST = up to 0.45 l hydrochloric acid / m^2 plated surface

Average consumption of hydrochloric acid for Direct Auto Rom was 0.25 l / m^2

For other chemicals (degreasing solution, leveling agent, brightening agent, purificator) Figure 3.2 compares usage at Direct Auto Rom before and after PP2 implementation.

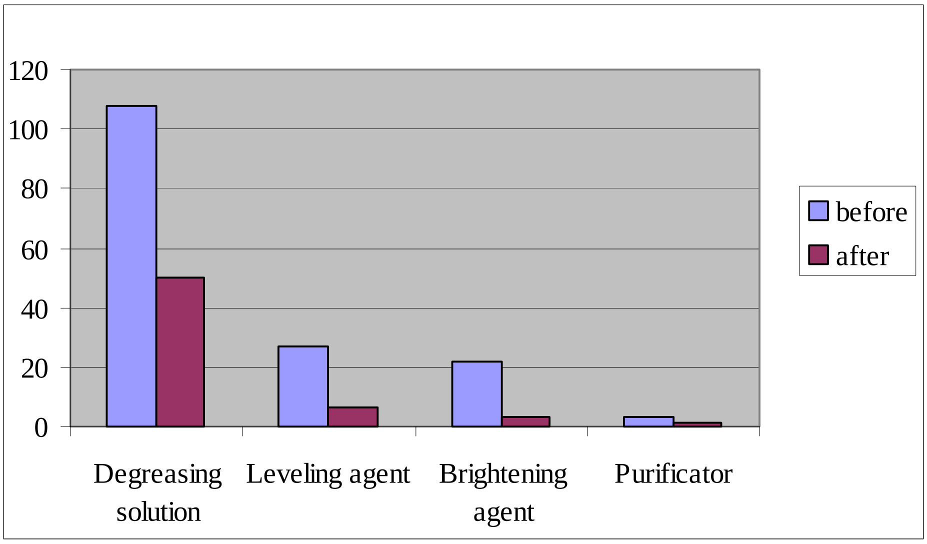


Figure 3.2 Chemical Use Before and After PP 2 Implementation

Chapter 4

Reducing Energy Consumption At Plating Processes

4 REDUCING ENERGY CONSUMPTION AT PLATING PROCESSES

Energy use represents a large portion of operating costs for plating enterprises. Reducing energy use offers considerable cost saving and environmental benefits. Energy reduction is the focus of international environmental legislation. As Romania aligns its legislation with EU legislation pressure on industry and the plating industry to improve energy efficiency will increase.

Energy Use in plating Factories

Main activities that consume energy within plating processes include:

- Heating technological baths and hot rinse stages;
- Electro plating processes;
- Plating solution maintenance (continuous filtering, cooling if necessary);
- Ventilation;
- Room heating.

Heating of Baths

Heating of baths is necessary to improve the efficiency of plating processes. Continuous heating of baths is necessary during processing to overcome evaporative, structural, and fluid heat losses.

On a typical plating line more heat is required to compensate for waste caused by:

- Higher than necessary ventilation rates
- Inaccurate temperature levels caused by thermometer pockets being coated with participates
- Uncontrolled cold water make of hot rinse tanks
- Insufficient hold time to reduce solution drag out with the work piece.
- Lack of tank insulation.

- This waste can easily be overcome by:
- Regular preventative maintenance
- Better controls
- Optimising processing times.

Plating Electricity Use

For electroplating low voltage direct current is provided via transformer rectifier sets. Modernised plants use efficient and controllable rectifiers

Electricity consumption for plating can vary considerably depending on the size of the work piece, stages and thickness of plating required and plant design and operating practices.

The largest uncontrolled power loses occur where

- Variable resistors are used to control the plating voltage
- More than one tank is supplied from one power supply, as a result over plating can occur.

- Excessive lengths of busbar and inadequate cross-sectional area of busbar and inappropriate busbar material selection.

Power losses can amount to 20 – 30% of power purchased

Extract Ventilation

Extract ventilation systems are often necessary at plating baths to improve the working environment and remove noxious fumes. However depending on the bath solution and hours of use they are not always necessary. The correct level of extraction should be provided to comply with regulations and provide an acceptable working environment.

Excessive extract ventilation results in:

- Electric fan motors running longer than necessary increasing energy bills
- Excessive air and heat extracted from the shop increasing the shop heating bill
- Increased maintenance of the extract ventilation system

Extract ventilation systems are often oversized with little or no extraction rate control. Systems should be controlled to provide just enough ventilation. Table 4.1 provides details of where extract ventilation is required and max ventilation rates for designing systems.

Table 4.1 Local Extract Ventilation for Zinc Plating

Stage	***Working temperature***	***Need for local extract ventilation***	***Max extraction rate per free surface area m3/h/m2***
Alkaline degreasing	< 60 ^{0}C	No	
	> 60 ^{0}C	Yes	2700
Pickling	< 30 ^{0}C	No	
	> 30 ^{0}C	Yes	3600
Alkaline zinc plating	Any type	Yes	3100
Acid zinc plating	Any type	Yes	3100
Activation	Any type	No	
Passivation	Any type	Yes	3100
Hot rinse	< 60 ^{0}C	No	
	> 60 ^{0}C	Yes	2300

Chapter 5

Treatment and Disposal of Wastewater from Zinc Plating Processes

5 TREATMENT AND DISPOSAL OF Wastewater FROM ZINC PLATING PROCESSES

There are over 500 plating enterprises operating in Romania and the majority of their wastewater treatment plants are in poor condition.

This section of the guide provides guidance to assist enterprises with improving their wastewater treatment. The guidance

- Provides an overview of the wastewaters from plating processes
- Provides an overview of wastewater treatment processes
- Provides an overview of the standards required to discharge treated wastewater to sewer
- Demonstrates that wastewater discharges from plating processes should be reduced prior to investments in wastewater treatment plant improvements
- Demonstrates the impact of reduced wastewater discharges on the size, capital and operating costs of wastewater treatment plants.

Sources and characteristics of wastewater

Rinse Wastewater

During plating operations rinse operations after the various plating operations discharge continuously. The characteristics of these wastewater streams are outlined:

- Wastewater with alkaline pH (post-degreasing)
- Wastewater with acid pH and Fe (post-pickling)
- Wastewater with acid / alkaline pH and Zn (post-zinc plating)
- Wastewater with acid pH and hexavalent Cr (post-passivation)

Spent Solutions

Solutions used in the plating process are discharged / disposed of intermittently. The characteristics of these spent solutions streams are outlined:

- Spent solutions with alkaline pH and oils (degreasing)
- Spent solutions with acid pH and Fe (pickling)
- Spent solutions with acid / alkaline pH and Zn (zinc plating)
- Spent solutions with acid pH and hexavalent Cr (passivation)

Treated Wastewater Discharge standards Romania

The limits for wastewater discharges into municipal sewage system or directly into wastewater treatment plants are in accordance with the values established by GD 188/2002 for the approval of norms regarding wastewater discharge into aqueous environment – Norms regarding conditions for wastewater discharges (NTPA 002/2002).

- pH = 6.5 – 8.5
- CCOCr = 500 O2 mg/dm3
- Cr total = 1.5 mg/dm3
- Cr 6+ = 0.2 mg/dm3

- Zn^{2+} = 1.0 mg/dm3

These standards are stringent and to achieve these standards wastewater treatment plants utilize flocculants to improve metals removal.

Another option is water recycling into zinc-plating technological flow if water characteristics allow this. The necessary water characteristics (in terms of conductivity less than 800 μS) can be achieved by mixing in certain ratio fresh water and recycled water.

Wastewater Treatment

An overview of the separate wastewater streams and wastewater treatment requirements for a zinc plater is provided in Figure 5.1.

Wastewater treatment includes the following stages

- Cr^{6+} to Cr^{3+} reduction;
- Metal precipitation (Zn, Cr);
- Settlement;
- Water recycling / discharge;
- Sludge treatment.

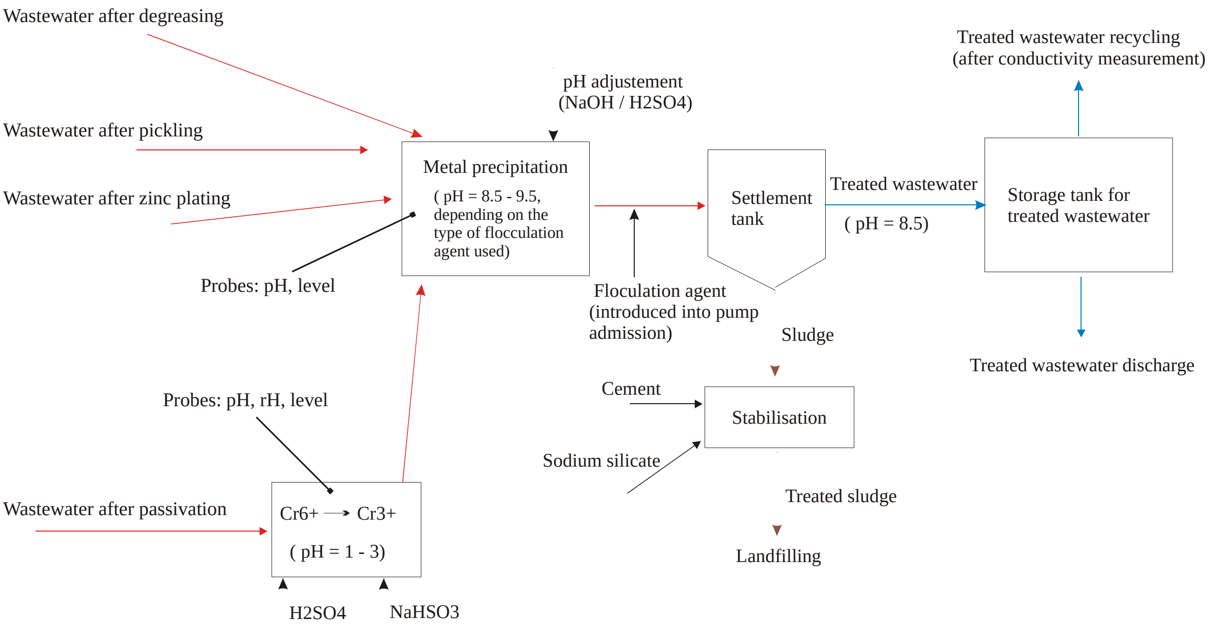


Figure 5.1 Wastewater Treatment Flow

The Wastewater treatment plant includes the following:

- Tank for collecting wastewater with Cr^{6+} and its reduction to Cr^{3+};
- Tank for collecting acid and alkaline wastewater and metal precipitation;
- Pump for water discharge and supply with flocculation agent;
- Settlement tank;
- Tank for treated water storage and pump for its recycling / discharge;
- Equipment for sludge filtering;

- Pump for sludge discharge and equipment for its treatment;
- Reagent tanks (H_2SO_4, NaOH, reducing agent, flocculation agent);
- Probes and electro-valves;
- Control panel.

Wastewater treatment plants can be designed to treat wastewaters using a store and batch treatment basis or to treat wastewater using a continuous flow basis treating wastewater as it is generated. Batch processes are usually manual operated plants treating wastewater on a continuous flow basis are usually automatically controlled.

The size of a plant treating wastewater on an automatic continuous flow basis will be considerably smaller than a batch process and a packaged automatic plant is the usually preferred option

Working parameters for wastewater treatment processes are presented in Table 5.1.

Table 5.1 Wastewater Treatment Parameters

Stage	***pH (pH units)***	***Reaction time (min)***	***Probes***
Cr^{6+} reduction	2,0 – 2,5	15	- level - pH - RH
Metal precipitation	9,0 – 9,5	15	- level - pH
Settlement	–	180 – 240	–

The largest and most costly in the effluent treatment plant is the settlement tank. As a simple guide settlement times are around 3 to 4 hours and the size of settlement tanks is 3-4 times the hourly wastewater flow-rate. A comparison between the settlement tanks for Direct Auto Rom for a single rinse process generating 5500 l/h of wastewater and for the multistage rinse process installed (58 l/h wastewater) is shown in Figure 5.2.

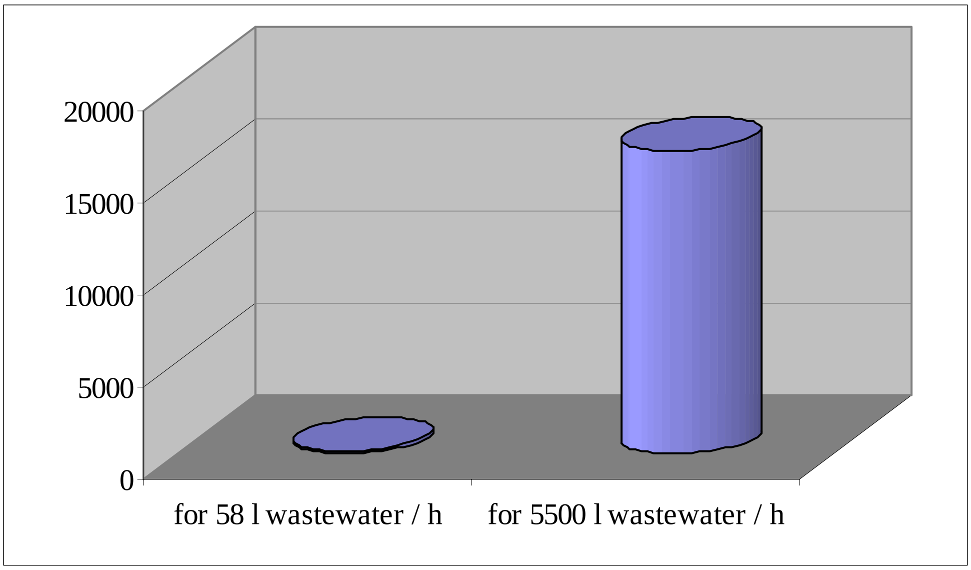
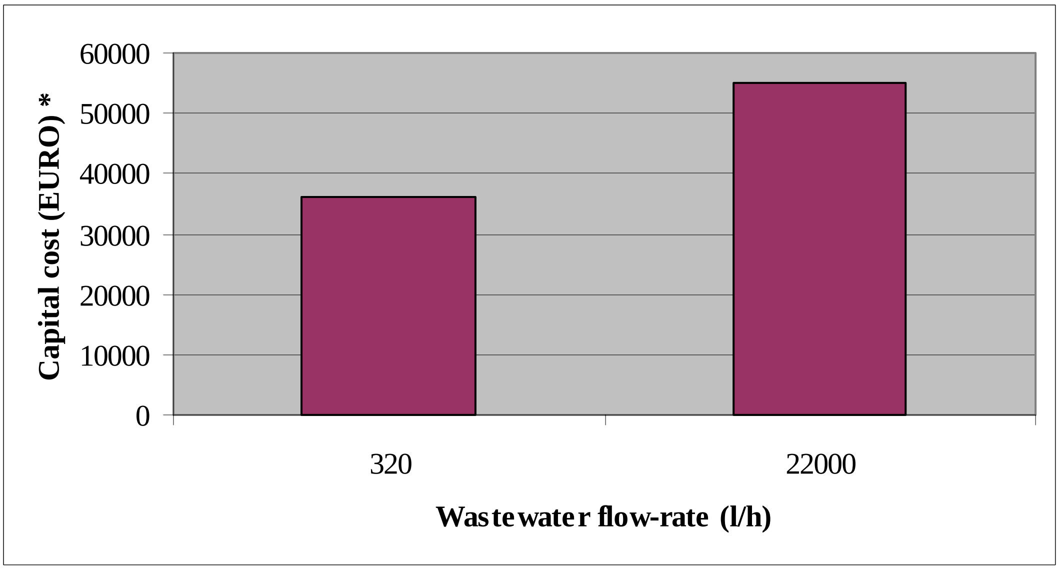


Figure 5.2 Settlement Tank Size Comparison

Figure 5.3 compares treatment plant capital costs for a plating shop with 4 plating lines similar to those installed at Direct Auto Rom and Timpuri Noi one plant treating wastewater from a conventional single rinse process lines and a water efficient process using multistage countercurrent rinsing.



* approximate values

Figure 5.3 Capital Costs Depending on Wastewater Flow-Rates

Reducing Chemical Use in Wastewater Treatment

Chemicals used in wastewater treatment and there purpose is shown below:

- Reagents for pH adjustment – HCl, NaOH;
- Reagents for treatment – Na2SO3 (Cr6+ reduction to Cr3+), NaOH (metal precipitation);
- Flocculation agents.

The quantity of chemicals used to treat metal plating process wastewater is directly related to the volume of wastewater generated and the metals content in the wastewater.

The efficiency of metals removal is increased as the concentration of metals in the wastewater increases.

Wastewater treatment chemicals can be reduced indirectly by:

- Minimising chemical carry-over into rinse water;
- Reducing wastewater volumes by for example using multiple stage counter-current rinsing
- Increasing the metals concentration in wastewater from carryover and rinsing by for example using multiple stage counter-current rinsing

.

Wastewater treatment chemicals can be reduced indirectly by:

- Designing and operating the wastewater treatment system to ensure accurate pH measurement and adjustment with good mixing of wastewater streams and good mixing in reaction vessels;
- Operating wastewater treatment to dose treatment chemicals only when required and with the minimum quantity required..

The impact of reduced wastewater volumes on the quantity of chemical reagents used and chemical reagent costs is shown in Figure 5.4. The columns compare chemical reagent consumption for the DAR plant with:

- 1 rinse stage (5500 litres rinse water / h for a carry-over of 1 l/h) as conventional system;
- 2 / 3 rinse stages (58 litres rinse water / h for a carry-over of 1 l/h) as installed.

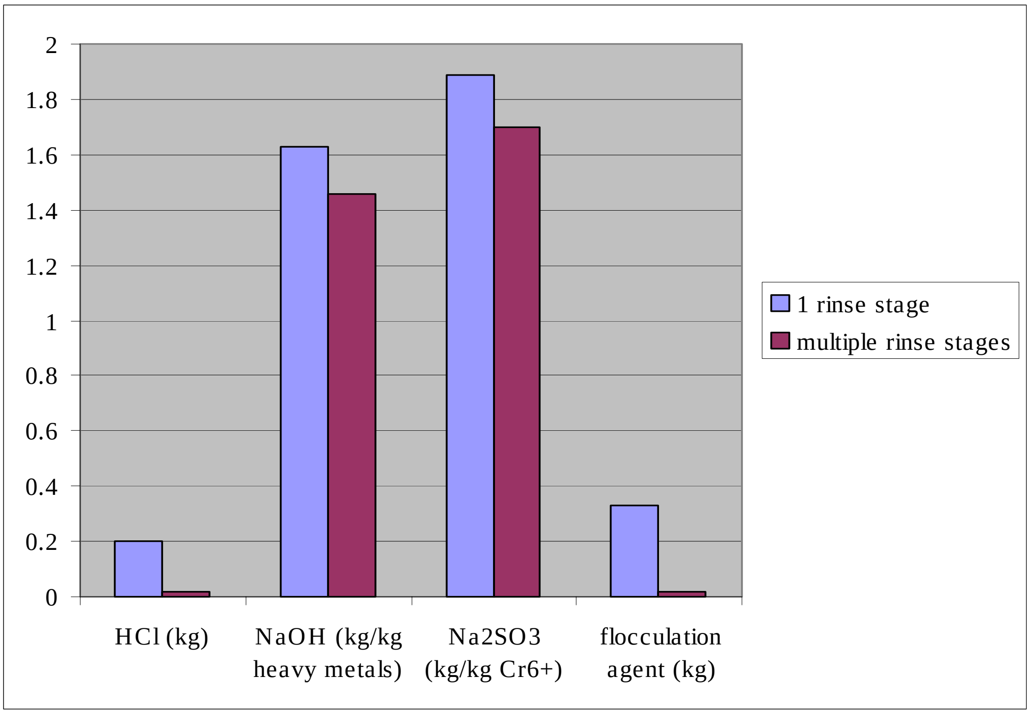


Figure 5.4 Reagents Consumption for Wastewater Treatment

The impact on running costs for wastewater treatment plants by reducing the quantity of wastewater to be treated is shown on Figure 5.5. Figure 5.5 compares the running costs for the Direct Auto Rom wastewater treatment plant as installed, treating wastewater from its multistage rinse zinc plating process, with the running costs for the same process with single stage rinses..

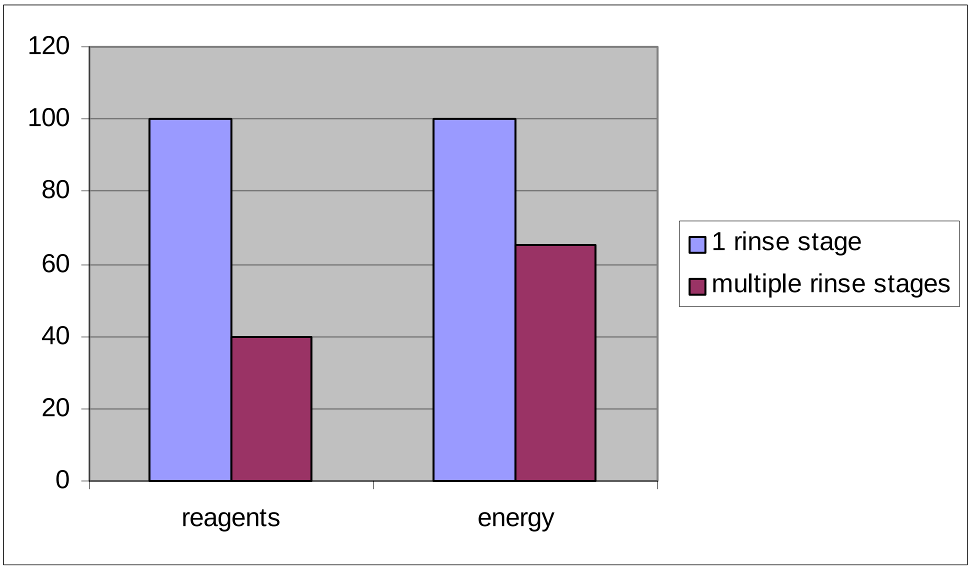


Figure 5.5 Treatment Plant Running Cost Comparison

Chapter 6

Treatment and Disposal of Sludge from Wastewater Treatment

6 TREATMENT AND DISPOSAL OF SLUDGE FROM WASTEWATER TREATMENT

Introduction

The treatment of wastes such as spent solutions and wastewaters from electroplating generate metal hydroxide/oxide sludges (treatment plant residues) which are considered **hazardous** wastes and, if not subject to material recovery could be landfilled at a hazardous waste landfill facility. Such landfills do not currently exist in Romania and many such wastes are currently stockpiled. Best practice, as defined in EU landfill directives is to subject all hazardous wastes to treatment to reduce hazards prior to landfill.

In the case of the residues from treatment of metal finishing wastes / wastewaters, the optimum and most cost-effective treatment is stabilisation. Stabilisation of these treatment plant residues generally results in a final waste for disposal which is NON-hazardous and can be safely disposed of to non-hazardous waste landfills accepting non-hazardous industrial waste.

Two similar processes are available, “stabilization” and “solidification”, these processes are very similar in terms of technology and reagents and really only differ in that “solidification” results in a monolithic solid waste for disposal whereas “stabilization” results in a crumbly solid waste.

These processes involve the immobilisation of toxic compounds by:

- Chemical mechanisms: chemical reactions by which insoluble compounds are formed;
- Physical mechanisms: embedment in a crystalline network or in a polymeric matrix.

Following a stabilisation treatment, a waterproof material is obtained, that physically isolates the sludge from the action of rainwater or groundwater.

Solidification consists in the obtaining of a solid monolithic material, which is physically strong (resistant to compression) and has very low permeability.

Application of Stabilisation to Metal Finishing Treatment Plant Sludge

The main reagent is anhydrous powder of Portland cement. This combines with water from sludge, forming first a colloidal gel (binding phenomenon), then a monolithic structure which includes the toxic components from sludge (hardening phenomenon). This type of process is proper especially for treating sludge with high content of toxic metals, because the high pH of cement supports the precipitation of multivalent cations as insoluble hydroxides or carbonates.

Moreover, the alkalinity of cement contributes to the neutralising of possible present acid compounds from the sludge.

Other additives can be used (clay, lime etc.) in order to improve the physical characteristics of the product. The use of sodium silicate leads to a higher resistance of the links between solid matrix and toxic metals, hence to a better resistance to water action.

The nature of the interaction between the sludge and the reagents is complex, taking into account that many reactions take place simultaneously, especially in the case of sludge that contains different species of reactive pollutants. The most important reactions are the following:

- Reactions between sodium silicate and sludge: lead to the acid neutralising and to the almost total insolubilisation of multivalent metallic ions;
- Reactions between sodium silicate and certain compounds of fixing agent (calcium ion from Portland cement): lead to a gel structure that is able to embed water, ions and other residual compounds, by different physical and chemical mechanisms;
- Reactions between fixing agent and water: hydrolysis, hydrating etc.

All the above mentioned reactions, between the three components (fixing agent, sodium silicate, sludge) lead to a continuous solidification by which the physical properties of sludge are continuously improved.

The obtained product is in fact a mineral material that contains different compounds of the treated sludge. Its physical properties vary in a wide range – from those similar to a soft soil, to those similar to clay schist.

The main stages of the treatment process are as follows:

- Sludge homogenisation, by mixing process in a cement mixer type apparatus;
- Addition of reagents;
- Continued mixing of waste and reagents (for about 30 minutes);
- Allowing the resulting sludge / semi-solid waste to stand and “set” (become more solid with time);
- Complete hardening of the product – after about 7 days;
- Leaching tests, to test for leachable heavy metals and check suitability for landfill.

Typical quantities of reagents – sodium silicate, lime, Portland cement – are established in each case, depending on the sludge composition. Usually, they are in the following range of values:

- Cement — 100 – 300 kg/m^3 of sludge
- Liquid sodium silicate (1.54 kg/m^3 density) — 20 – 30 l/m^3 of sludge
- Hydrated lime — 0 – 100 kg/ m^3 of sludge

After mixing, the products are air dried until complete solidification; then leaching tests are performed in order to establish the level of chemical fixing of the metallic ions.

The optimum recipe is chosen taking into account:

- Leaching tests results correlated to the legal norms;
- Economic aspects, in terms of using the lowest possible quantities of cement, lime and sodium silicate.

Treated sludge is disposed of by landfilling in accordance with legal norms for waste disposal (Governmental Decision 162/2002 on waste landfilling, Order 867/2002 of Ministry of Water and Environmental Protection regarding criteria that must be accomplished by waste in order to be on a list of waste accepted on a certain landfill).

Chapter 7

Conclusions

7 CONCLUSIONS

- Waste minimisation has benefits both for environmental protection and for cost savings

- Waste minimisation can be achieved by minimising chemicals, water and energy consumption

- Consumption minimisation can be achieved by three main ways:
  - Technology improvements
  - Staff training
  - Management system improvements

- From the above mentioned ways, the last two can be realised with minimum costs

That is why . . . **DO NOT FORGET !**

☹ **Measure water, chemicals and energy consumption according to the production (plated surface) and working time, for different working conditions**

☹ **Assess running costs**

☹ **Compare the case in which you apply best practice procedures for water, chemicals and energy consumption minimisation with other situations**

☺ **The results will be encouraging !**

and

Train the staff, involve them in decision making and … stimulate them !

Measure, register data, compare results, analyse unusual aspects and implement measures for consumption minimisation and … profit increase !

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