7 Practical experiences with reducing industrial use of water and chemicals in the galvanising industry

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Abstract

While 'Soft' factors, like employee training, experience and work instructions can significantly reduce the consumption of water and chemicals by galvanising companies, further significant improvements can be achieved by technical measures. This article demonstrates that the reduction of water and chemicals use can yield significant financial benefits to a company, without compromising product quality or productivity.

Based on the results of a benchmarking survey, a systematic optimisation approach was developed to identify all options that help to minimise water consumption and the use of chemicals, and therefore also sludge generation, while at the same time saving the companies money.

Five case studies identified and implemented measures, including changing the rinsing technology in three pickling plants at the wire producer Joh. Pengg GmbH, the use of spent caustic for neutralisation and an electrolysis plant for copper recovery at the printed circuit board manufacturer AT&S, changing the rinsing technology in the production of printing cylinders by Rotoform and a reorganisation of acid management at the Mosdorfer hot-dip zincing plant.

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All these measures generally reduced wastewater generation by at least 40 % and the amounts of spent process chemicals that have to be treated by half. All measures paid back according to the financial investment standards used by the companies. The paper also discusses the optimal diffusion of this knowledge.

7.1 Galvanic industries and the environment

Galvanic surface treatment is crucial in modern engineering, producing cheap and durable, long-lasting surfaces. Over 10,000 galvanic companies and 8300 so-called in-house galvanics in Europe employ 440,000 people. This number includes the printed circuit board manufacturing industry.

Galvanic processes do, however, cause environmental problems for the companies using them. Galvanic companies generally consume large amounts of water, and the metal salts, acids and caustics applied in the processes have to be removed from the wastewater by expensive treatments before discharge.

About 1 % of the total hazardous waste in Europe is generated by galvanic companies. In 2002, the amount of sludge from galvanic companies in Germany was estimated to be about 80,000 tons annually. Older estimations indicate more than 250,000 t (1997) of sludge without including anodising and pickling companies. About 3 % of the sludges are used as secondary raw materials; the rest is landfilled. According to the Austrian Environmental Agency, about 10,000 t of hazardous and non-hazardous waste result from the Austrian galvanic industry (Sebesta 2002). The Styrian chamber of commerce reports that about 50,000 t of galvanic and hydroxide sludge is produced in Austria annually.

Analyses of companies with similar products show that their water and chemicals consumption varies greatly (Table 7.1).

An Austrian survey in 2001 arrived at similar results (Fresner 2000). Besides the technology employed, organisational factors like dripping time management, staff training or controlling the consumption of chemicals and water had a significant influence on the generation of waste in surface processing companies.

Table 7.1 Specific consumption of degreasing agents, pickling agents and electrolyte in electrochemical zincing in five German companies

	Treated surface area [m²/a]	Pickling agents used [t/a]	Specific consumption pickling agent [t/100,000 m²]	Electrolyte used [t/a]	Specific consumption of electrolyte [t/100,000 m²]	Cleaning agents used [t/a]	Specific consumption of cleaning agents [t/100,000 m²]
1	158,000	24.0	15.0	38.0	24.0	1.2	0.8
2	200,000	202.0	101.0	160.0	80.0	12.8	6.4
3	63,000	21.0	33.0	6.0	9.5	0.1	0.2
4	468,000	150.0	32.0	90.0	192.0	12.4	2.6
5	66,000	1.3	2.0	15.3	23.0	7.0	9.0

It was concluded from these results that there must be a large potential in many companies to avoid and reduce water and chemicals consumption and sludge production, while probably also improving their economic performance by saving expenditure on water and chemicals.

Galvanic companies apply a broad variety of processes, such as degreasing, pickling, etching, passivating, phosphatising, anodising, burnishing, electrophoresis painting, gold plating, silver plating, copper plating, chrome plating, nickel plating, tin plating, zinc plating, etc. The purpose of these processes is to produce a corrosion-resistant metal layer on a base metal or on a plastic surface through chemical or electrochemical treatment.

The parts are first introduced into an acid or alkaline bath to be cleaned, after which the electrolytic or chemical metallisation takes place. After each process bath, the components are cleaned by various techniques, using larger or smaller volumes of water, to avoid impurities being carried over to the next process stage.

The processes differ in the chemical composition of the process baths (degreasing, pickling with caustic soda solution, hydrochloric acid or sulfuric acid, solutions of different metal salts), as well as in their temperature and the use of electric current.

The process water therefore contains, at least to some extent, all process chemicals (degreasing agents, acids, bases, additives or metal ions) and hence has to be pre-treated before being discharged to a wastewater system. Typical wastewater treatment includes neutralisation and precipitation. These processes generate moist sludge, which is usually landfilled.

7.2 The vision of zero emission galvanising

Only integrated and almost closed production processes meet the present legal and economic requirements. Modern galvanic companies use water-efficient methods and reutilise a large part of their metals. As early as 1996, the authors of the ‘Rheinland-pfälzischen Branchenkonzeptes’ described their vision of ‘water-efficient galvanic companies’. ‘Process bath constituents are recovered by appropriate procedures and recycled back into the respective process baths.’

Although some German galvanic companies already meet these requirements, it should be remembered that these companies have been newly built, and most were financially supported by public authorities.

Most of the surface treatment plants in Austria are, on average, 10 to 15 years old. These plants face the problem that the process layout is not designed for a water-efficient and zero waste operation.

Obstacles to the revamping of existing plants often include space problems and the uncertainty whether production after the revamping operation will run smoothly and, especially, without quality losses. In addition, each revamping operation usually means a major financial burden to the enterprise, since capital costs are high and production has to be suspended during the re-equipment phase, leading to additional costs. Production stops are a major problem particularly for so-called ‘in house’ galvanics, since the plants can become bottlenecks to other departments during the reconstruction.

The variety of technologies available for the reduction of wastewater quantities, the recovery of constituents and the maintenance of baths often makes it difficult for companies to select the most appropriate process. Technologies include:

- treatment of process baths with membrane filtration, ion exchangers, electrolysis and thermal processes to achieve a long lifetime for the process baths;

- retention of bath ingredients through appropriate processes like transporting goods with little drag out, splash guards or optimised composition of the baths;
- multiple use of rinsing water through appropriate processes like cascade rinsing or closed water cycles through ion exchangers;
- use of processes for the recovery of raw materials and supplies from process baths or rinsing water (dialysis for nickel, evaporation of chromium, precipitation of zinc);
- substitution of raw materials hazardous to water;
- separate collection and treatment of process wastewater, especially of acid and basic wastewater flows as well as chromium-containing, cyanide-containing, nitrite-containing, precipitating and sulfate-containing wastewater flows.

Experience gained with these measures shows, that improving the ecological situation does not necessarily mean a financial burden. In fact, considering all advantages and savings, ecological measures often lead to economic advantage. The purpose of the ZERMEG project was to help improve the eco-efficiency of enterprises by identifying all measures that are at the same time ecologically and economically efficient and thus motivate companies to implement simple measures which reduce the environmental effects of galvanising.

7.3 ZERMEG: Zero Emission Retrofitting

The ZERMEG approach was developed to address the above problems. The ZERMEG project was carried out within the framework of the Fabrik der Zukunft (‘Factory of the Future’) programme, and was commissioned by the FFF, the Austrian Research Funds, and BMVIT, the Austrian ministry for innovation and transport. ZERMEG stands for ‘Zero emission retrofitting method for existing galvanising plants’ (see www.fabrikderzukunft.at). ZERMEG’s aim is to define a method to achieve an in-depth analysis of surface processing companies. It provides a guide to help collect data, interpret them and provide ideas for improvement. It also offers a guide for bath maintenance and for closing water cycles, as well as a guide for the implementation of measures to modernise galvanic plants in such a way that

- the amounts of wastewater produced and the pollutants content of the wastewater are minimised;
- constituents of the baths can be recovered;
- non-reusable waste can be recycled by other companies and sectors.

ZERMEG specifically wants to assist in the identification of all measures that have the potential to reduce waste and emissions from a process, and are economically feasible at the same time.

ZERMEG wants to meet these requirements by:

- using a methodical approach;
- providing support by calculation programs;
- providing support by producing reference data and standardised descriptions of technologies;
- offering a discussion platform for an exchange of experiences, for the further development of the model and for the diffusion of data (www.zermeg.net).

7.4 The methodical approach in ZERMEG

The methodical approach divides the analysis into 9 steps: see Table 7.2.

Company analyses in Cleaner Production projects like PREPARE or ECOPROFIT have shown that even in the analysis phase, many effective measures can be implemented with little investment (see: www.prepare.at; www.oekoprofit-graz.at).

Table 7.2 The ZERMEG method

Step description	Activities	Potential for optimisation
1. Analysis of current situation: Measuring water and chemicals consumption	Creating a flow chart, documenting water consumption using a meter, documenting the consumption of chemicals using data from the accounts department, implementing bath-specific documentation of chemicals consumption	Missing data, implementing indicators, daily concentration measurements, avoiding single chemicals where possible
2. Analysis of current situation: Detecting drag out	Measuring, calculating or estimating	Short drain times & exchange times, broad part spectrum, improving the assembly of the parts, base-frame geometry
3. Analysis of current situation: Defining rinsing criteria	Target values from the literature for rinsing criteria and/or conductivity of the last rinsing water; calculating the rinsing criteria used	Quality control, reducing the amount of water, measuring conductivity to control the amount of rinsing water, manually controlling the amount of rinsing water
4. Calculation for comparison: Calculating water consumption	Using the ZEPRA program[a]	Comparing with actual water consumption, volume of rinsing loads, rinsing technologies
5. Calculation for comparison: Calculating chemicals consumption	Using the program	Comparing with actual consumption. If deviations are found: identifying loss flows, technical measures to lengthen lifetimes
6. Defining options for external disposal and recycling	Contact with potential customers and suppliers	Identifying by-products
7. Defining options for possible external recycling	Using the register of water cycle closing technologies	Recycling constituents of baths
8. Evaluating options	Evaluation by financial and sustainable criteria	Pay-back calculations and sustainability evaluation of alternatives
9. Optimising the wastewater plant		

[a] ZEPRA was programmed in MS Excel by DI Gwehenberger (Graz University of Technology - RNS) and DI Christoph Brunner (Joanneum Research, Institute for Sustainable Techniques and Systems).

The internal analysis of the galvanic process improves staff awareness of problems and leads to critical reflection on operational practices. There are a number of important questions the operators have to ask: Are all the additional ingredients actually necessary? What purpose do they have? Do all the baths operate at constant and optimal conditions? Are the rinsing water volumes necessary?

The answers to these questions often yield surprising results. For example, the substitution of some organic bath ingredients can have a positive effect on the organic load of the wastewater as well as on the amounts of galvanic sludge.

All incoming and outgoing material flows should be recorded in as much detail as possible. The following questions should be answered:

- Where are the largest volumes of chemicals in the process?
- Where is water used and how much rinsing water is used?
- When and why are concentrates/semi-concentrates discharged?
- What is the consistency of the data?

The recorded mass flows over a representative period of time are entered into a data sheet. The following data sources are relevant in practice (Table 7.3):

Table 7.3 Data sources for the description of material flows

	Data source
Water	Calculation of water consumption by the accounting department, meters and records
Chemicals	Accounting department, records

Since the correlation between mass flows of chemicals and water and product volumes is also important, the throughput of parts has to be recorded. In order to calculate specific indicators, it is necessary to record the surface areas processed. The surface-related consumption rates of water and chemicals are essential instruments for the identification of measures to reduce consumption.

Additional information must be collected about existing process water flows from the galvanic line to wastewater treatment facilities. These data are the input for the further stages in the process and a reference for later comparisons.

7.5 The ZEPRA program

The ZEPRA program is a tool to minimise the unproductive output of galvanising tanks. It was first developed and tested in a small anodising factory. This computer-based tool had to meet a variety of conditions:

- It had to be applicable to different companies;
- It had to allow quick calculation of variants to the existing process;
- It had to produce a visually appealing output;
- It had to be able to get results without precise knowledge of chemical reactions (working with rules of thumb, experimental data, experience);
- It had to be able to calculate sludge composition to find opportunities for its further use;
- It had to calculate the composition of wastewater to find opportunities for closing water cycles or removing valuable components;
- It had to be easily adaptable to incorporate new knowledge;
- The companies' experts had to be able to use it without intensive training.

Considering these requirements, it was decided to program a new tool using Visual Basic for applications based on Microsoft Corporation's Excel program, rather than using standard software. Standard flow sheeting programs are difficult to integrate with a knowledge base, and standard life cycle analysis software is not suitable to consider recycles and the integration with heuristics regarding chemical reactions.

Excel is a well known spreadsheet program already in use in most companies. The original macro language used in Excel has developed into a programming language that is very similar to BASIC, and can be used for fairly complex programs. Most data can be entered and edited in traditional spreadsheets, while complex calculations are programmed in Visual Basic.

The program represents the flow of materials through the plant, representing the individual process steps by black boxes connected by material flows. One batch corresponds to one program run. It is assumed that the first run of the program uses tanks that have the default concentration supplied by the operator of the plant. This situation, though unrealistic for an existing plant, enabled us to calculate the lifetime of batch units like static rinses. Each additional run uses the concentrations of the previous run, so that after a few runs we get a realistic status of the plant. After each run, the plant status is saved, so it is possible to start at any given point, for example after 100 charges. It is also possible to add or subtract separators for cleansing tanks and/or recycling loops. (See Figure 7.1).

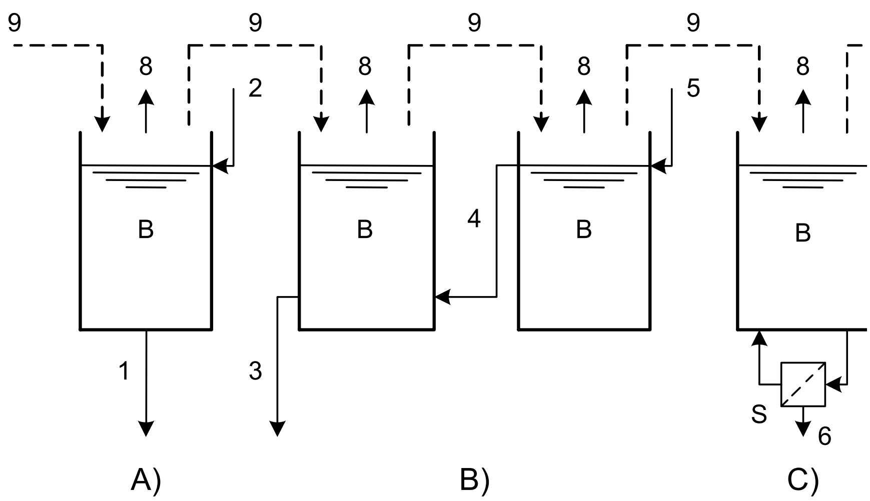

Figure 7.1 Three examples of water flows entering and leaving a bath. All three cases can be calculated with one tool

A) Static tank: batchwise discharge every few hours to every few months; batchwise refill and continuous or discontinuous compensation of evaporation (flow 8).

B) Counter-current rinsing cascade: continuous discharge; overflow from bath to bath; continuous freshwater supply.

C) Bath with some kind of purifying apparatus: continuous or discontinuous wastewater / sludge flow from purifying apparatus (e.g. a membrane filter); continuous or discontinuous compensation of evaporation and compensation of water loss via sludge (flow 6).

A few flows are common to all kinds of arrangements: evaporation, dragout into and out of the baths with the processed items (flows 8 and 9).

Each tank and separator is regarded as one unit and is represented by a single spreadsheet. The flows out of such a unit are the input for other processes. Each unit is regarded as a black box, in that what is happening inside this box does not affect other units, which only see the input and/or output. The output flows are calculated from the input flows in basically three different ways.

The best scenario is one in which all chemical or physical reactions that take place in a tank or separator are known. In this case, it is possible to provide exact output calculations. For most cases, this implies that all the components in the input flows have to been known as well. This is the only way to get theoretical results that are comparable to real measurements. However, even if the main reactions are known, most cases will in fact have to rely on a second-best option.

The second-best option is one in which experimental data of comparable process steps are available, which can be fitted to the actual design of the unit under analysis. In most cases, the results obtained by this way are comparable to results from theoretical models.

Sometimes even the experimental data are missing. In this case, a rule-of-thumb approach must be used, based on the experience of people working at the unit. This includes information like ‘we add 50 l of water per day’, or ‘about a quarter of the chemical is replenished every other week’. These data will yield adequate results for the first assessments, but for further work they will have to be replaced by accurate measurements.

This program is being designed in an open way. The simulation of unit operations that are present in all galvanising plants, like cleaning tanks and rinses, is well advanced. Further unit operations that have already been completed are tanks of anodising plants and steel pickling. However, there are many different galvanising plants and little is known of the chemical processes involved if there are impurities in the chemicals or the water and if the material is a composite alloy of many different metals. As soon as we have experimental data on chemical reactions, they will be incorporated into the program.

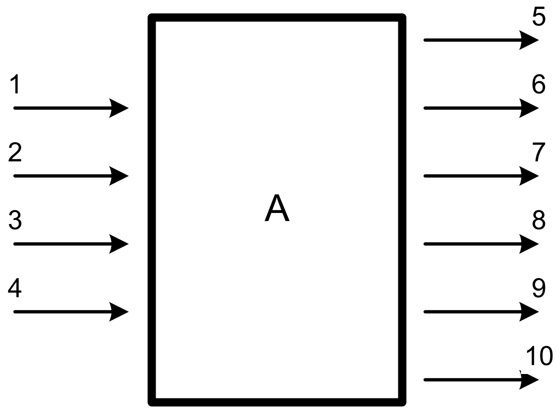

Figure 7.2 Input and output flows per process unit. The black box A is connected to other processes by inflows (1) materials input; (2) water input; (3) dragout input (with material); and (4) recycling stream from process X; and by outflows (5) evaporation; (6) processed materials output; (7) water overflow; (8) dragout; (9) recycling stream to process Y; and (10) sludge/oil/suspended matter

Each process is regarded as a black box A, see Figure 7.2. The processes in this box are chemical, physical or biological reactions. If the detailed reaction is known, the relevant equations are used to calculate the output flows from the input streams. If the exact reactions are unknown, we have to rely on empirical data or our own measurements.

7.6 Using the program

The first step towards improving water efficiency in a galvanising plant involves a thorough analysis of the consumption of water and chemicals in the various process steps. These data can be derived from accounting data, such as the amounts of chemicals bought, or from on-site measurements and asking people who work with the equipment. If the company being analysed has an adequate environmental management system, these figures are relatively easy to find, otherwise it may take a while to obtain the necessary data.

The existing plant is then modelled using the ZEPRA computer program, which automatically generates a speadsheet for each tank. The values of all known input and output flows, the default concentrations of all tanks and other tank-specific values, e.g. rinsing criterion, are entered into the Excel worksheets during the first run, which can be regarded as a setup run. The input to the first tank yields the concentration for the output flows of the first tank. These values are used as input for the second tank and so on, until the preliminary plant has been set up. In subsequent runs, each one representing one lot of material through the plant, the values are calculated using the values of the previous run. All data are saved after each run, so that later sessions can start at a particular state of the plant. After a few runs, it is possible to compare the calculated values with the values obtained by measurement. The calculated values represent the theoretically feasible best consumption values. If he actual values are lower than the calculated ones, one has to assess whether all quality criteria, e.g. rinse criteria, are being met by the current operation in the plant. In most cases, the measured values will be higher, sometimes substantially so, than the calculated ones.

This is followed by the final step, that of interpretation and identification of measures. As a virtual plant has now been created in the computer, parameters can be changed without influencing actual production. It is possible to add or remove tanks, and to add separators to simulate wastewater reuse in other tanks, or add separators to obtain marketable by-products. Some of these alterations simply will not work, but others will, at least in theory. This can be followed up by running traditional experiments in the laboratory to find possible solutions to the problem of reducing the unproductive output of galvanising plants. The main advantage of using this program is that it offers the opportunity to exclude impossible solutions before starting laboratory experiments and perhaps to find unusual solutions not yet tried elsewhere.

The evaluation of the actual situation in terms of plant configuration and material flows should finally lead to the following results:

- transparency of the whole galvanic process, including wastewater treatment, in terms of existing material flows and their relevance to waste generation;
- identifying the main source of relevant material losses;

- identifying processes with high rinsing requirements;
- identifying process baths with a high dumping frequency.

Surface-related data about consumption and the concentration of chemicals are important indicators for optimisation. On the one hand, they represent the basic information for daily monitoring, and on the other hand, they provide the basics for the analysis of problems and options for improvement (Fresner et al. 2002). The actual losses due to dragout can be identified by on-site tests in the company, in which a certain number of products or racks are rinsed in a defined rinsing tank, at the usual conditions, and the rinsing water is analysed afterwards.

We regard this approach as a vision-driven approach, which identifies the ideal end result as a starting point for optimisation. This ideal end result is defined by the appropriate rinsing criteria, minimal dragout, optimum useful bath time, economically feasible measures for recycling and maximum external use of spent solutions. This vision can serve as a long-term objective to focus the decisions about possible options for change towards the most useful ones, given the greater picture of the ideal feasible result. This sequence guarantees that the most effective

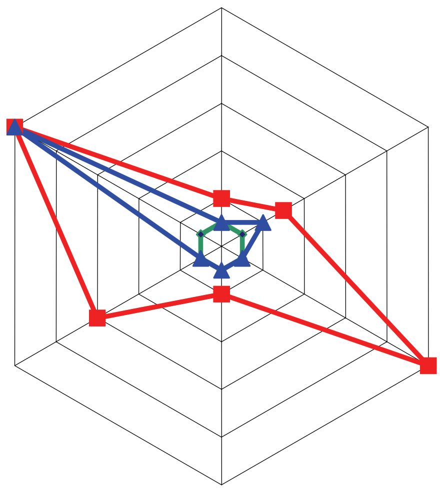

Figure 7.3 This figure shows the ZERMEG Grid for the six basic parameters in the case of the Heuberger anodising plant (see below), to compare the initial situation (outer line) with the results of the optimisation (middle line). The ideal values are represented by the central hexagonal line

measures which at the same time require the smallest investments and operating costs are selected first (Fresner 2004).

We have also developed a tool for the evaluation of the quality of galvanic processes: the ZERMEG Grid. It uses a spider plot with six poles, at which the following parameters are represented by the ratios between their actual values and the ideal values: rinsing criteria, dragout, rinsing water consumption, material losses in pickling, useful lifetime of process solutions and the ratio between external recycling and the reuse of the spent process solutions. The instrument provides ideal values for these parameters (see Figure 7.3).

Since the development of ZERMEG focused on understanding the processes involved in pickling and degreasing various metals, a detailed literature search was undertaken to describe the factors influencing the quality of pickling and degreasing and to prepare models for use in the calculations.

7.7 Case studies

Case study: Eloxal Heuberger

This company with its 24 employees is a typical representative of small to medium-sized Austrian companies. The number of employees has increased from 15 to 24 in recent years, and production has increased from 20,000 m^2/year to 90,000 m^2/year over the last five years.

The company anodises aluminium surfaces, a process in which the aluminium surface is converted to an oxide film (see Figure 7.4). The resulting dense and hard surface is perfectly connected to the base material. It protects the anodised aluminium to a large extent from corrosion and abrasion. Almost all aluminium alloys can be anodised. The enterprise processes parts of highly diverse origin: profiles for facades, windows and solar plants, sheet metals, but also many small articles (parts for transmissions and engines, exhaust systems, bicycle parts, fine mechanical engineering components and medical technology components).

Since the oxide coatings are heavily dependent on the composition of the material, prior surface treatment must be adjusted to the material to

Figure 7.4 The anodising plant at Eloxieranstalt A. Heuberger GmbH

be treated. This includes an intensive degreasing of the parts, which may enter the factory in an oily or greasy state. Different procedures are used to produce different oxide coatings, which have to meet certain decorative and functional requirements.

The present study determined the average grease and oil film on the materials as they were delivered to the plant by the customers. It was found that burnished and polished parts were practically grease- and oil-free, while mechanically treated parts and sheet metals had an average oil cover of approx. 1 g/m^2 surface.

After degreasing in a light alkaline bath, the parts are pickled in caustic soda solution to produce a metallic surface. After pickling, the parts are rinsed. This is a critical process, since the adhering pickling solution must be completely and relatively rapidly removed from the work pieces, in order to avoid the so-called 'after-pickling' effect, which would lead to uneven surfaces. Since the pickling solution is very viscous, a relatively thick liquid film sticks to the surface when the parts are taken out of the pickling tank.

We assessed the dragout using more precise measurements. It was shown that the drag out after the pickling were several times higher than was originally expected.

After rinsing, the aluminium parts which have to be processed are immersed in an electrolyte consisting of sulfuric acid. Direct current is then used to produce an oxide coating. Different electrolyte, current and bath parameters yield different characteristics of the resulting surface layer.

After anodising, the parts are again rinsed.

After a final inspection, the parts that are ready for delivery are examined for their technical and decorative quality. The finished parts are carefully packaged.

We introduced detailed records to the plant, which had to be documented on a daily basis: water consumption; energy consumption; chemicals consumption; measurements of the effects of bath concentrations on the basis of daily analyses; discharge rates of the baths; special observations.

This allowed us to point out the following weak points:

The actual dragout – particularly after the pickling – was greater than the theoretical value. This was caused partly by the fact that the pickling solution is very viscous, and partly by metal losses being substantially higher than expected, because some parts were pickled several times to render the surfaces metallically bright again after errors in the subsequent galvanic treatment. Good housekeeping measures (improvement of work instructions and increased control) and intensified control of bath conditions (temperature and chemical concentrations) allowed the error rate to be significantly reduced, from 4 to less than 2% of parts.

With the existing rinsing configuration, the actual amount of rinsing water needed to meet the desired rinsing criterion clearly exceeds the theoretically required value. Concentration profile measurements in the rinses showed that the high density of the media and the partially poorly functioning circulation of the rinses (driven by compressed air) cause a pronounced concentration profile in the rinses[11.] Improved bath circulation by compressed air and the introduction of a constant circulation even during production stops could achieve a clear improvement, in the form of a reduction of the concentration differences.

The anodising baths also showed a significantly increased consumption of sulfuric acid. This proved to be caused by the retardation plant for the extraction of dissolved aluminium. The retardation plant is based on the principle of differential surface absorption of sulfuric acid and aluminium on a resin. This resin was very old at the beginning of the project, and was replaced. This led to a clear improvement of the performance of the plant, and to a significantly reduced acid discharge. These two measures managed to reduce sulfuric acid by more than 30 %.

The program was used to calculate the evaporating water quantities in relation to the temperature and air speeds in the hall. This showed that with the quantities of water used currently, evaporation from the baths is only a small part of the total water consumption. The evaporating quantities could only play an important role in the future if the consumption of fresh water could be clearly reduced.

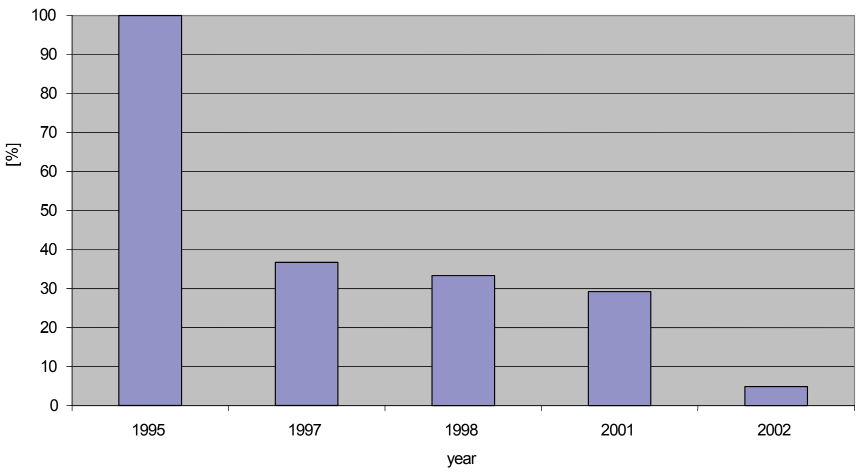

Figure 7.5 Specific water consumption at Eloxal Heuberger (Heuberger GmbH 2002)

Before the study, direct cooling was used for the anodising tank. In order to reduce the huge quantities of cooling water required to keep the temperature of the anodising baths within the required range, a closed cooling cycle with integrated refrigerators was designed. This uncoupled the cooling water quantity from the amount of rinsing water, resulting in an adjustable, tailored amount of rinse water. The investment required for this was approx. 100,000 euros, while the amount saved by reducing water consumption for an annual production of 90,000 m² was approx. 27,000 euros. This calculation does not take the throughput increase and the quality improvement into account. Meanwhile, the specific water consumption could be reduced to less than 40l/m². Some quality problems arose, which were due to the rinsing technology applied. These errors were examined with the help of a metallurgical expert, in order to explain their causes.

We tried to describe and define errors in the starting material, errors in the mechanical pre-treatment and pickling and rinsing errors more precisely, in order to allocate errors. This also served as a basis for additional training activities in the enterprise and considerations for automated control of the water flow through the rinses.

The results show that progress is promising (Figure 7.5). The consumption of acid and caustic solution per treated surface was decreased by around 50 %. This was achieved by the following measures:

- better understanding of the processes in the baths;
- better understanding of the relevant operational sequence;
- better modelling and data collection;
- expertise-building in the enterprise;
- optimising the degreasing tank;
- minimising the metal erosion to achieve the desired effects;
- optimising and considerably extending the lifetime of process baths;
- optimising the use of new technologies for bath maintenance;
- identifying new recycling options.

AT&S

At their plant in Fohnsdorf (Austria), AT&S produce printed circuit boards for cars and mobile phones. As the process plants are changed frequently, the project focused on optimising the wastewater treatment plant. Two options were identified:

- electrolysis of copper to recover copper from concentrates;
- use of caustic stripping solutions for the partial neutralisation of acidic concentrates.

The etching of printed circuit boards generates copper-containing concentrates and rinsing water. Baths of sodium persulfate are used to clean the surfaces and activate them. Depending on the process, an 0.5 to 2 µm layer of copper is dissolved. This copper has to be precipitated in the wastewater treatment plant, and residual persulfate has to be reduced.

An electrolysis plant is an appropriate technology to electrolytically separate the copper from the wastewater. The copper is collected in a very pure form as balls and can then be recycled. At the same time, the persulfate is reduced. The benefits of electrolysis are: minimisation of hydroxide sludge; saving reducing agent; recovery of copper.

A drum electrolysis cell was selected, in which the copper precipitates onto rotating copper balls. The concentration of residual copper is as low as 0.5 to 1.5 g/l. The benefits of this cell are its good hydrodynamic properties and a high electrical efficiency of up to 70 %. The project would not have been feasible if a new plant had had to be bought, but because another plant had shut down, a used, but practically new electrolysis plant with matching capacity could be acquired. The revenue from the recovered copper, the savings on wastewater treatment chemicals and the reduced sludge for disposal resulted in a static payback time of 15 months.

The strongly caustic stripping solutions were purified in the past using filters and an ultrafiltration plant, before being neutralised with hydrochloric acid. In the new situation, the caustic concentrates are used for the partial neutralisation of acidic concentrates in the wastewater treatment plant. Annually, this saves approximately 20 tons of caustic soda and a similar quantity of hydrochloric acid.

Joh. Pengg AG

The firm of Joh. Pengg AG in Thörl (Austria) specialises in the production of wires for sophisticated applications in the automotive, electric and machine manufacturing industries. These products have to have very precise dimensions, and have to meet strict requirements regarding their mechanical parameters. The company is certified according to VDA 6.1, ISO 9001 and QS 9000.

The production of the wires is done in several steps, three of which are galvanising steps. it was these three (batch pickling plant and two continuous pickling plants) which were analysed in this project.

Initially, a wire rod is pickled in a batch plant using hydrochloric acid. After pickling, it is rinsed in a two-step rinsing cascade using cold water. The next step consists of rinsing in hot water in a hot-water tank, followed by phosphatising and rinsing in the hot-water tank. After drying and drawing, the wires are heat-treated, followed by continuous pickling and phosphatising in two plants, depending on the dimension of the final wire. Calculations showed that the consumption of rinsing water could potentially be reduced by up to 80 % in the static pickling. It was decided to change the rinsing technology by combining the two-stage rinsing cascade with the static hot-water rinsing tank to form a three-stage rinsing cascade.

In practice, the volume of rinsing water in the static pickling was reduced by 50 %. As a next step, the rinses in the continuous pickling plants are currently being separated into three-stage rinsing cascades.

In parallel with these studies, a concept was developed in recent months to process the spent acids into a by-product which will be used by another company.

Mosdorfer GmbH

The Austrian hot-dip zincing company Mosdorfer, located in Weiz, produces components for electricity suppliers, and has 30 employees. Mosdorfer is a renowned specialist in this sector. It has developed from a forgery into an innovative partner of companies in the energy, railway and telecommunications sectors.

In the hot-dip zincing plant the following products are processed: components for high- and medium-voltage energy suppliers; insulators; dampers and spirals for electrical installations.

The following baths are used in the zincing plant: degreasing with a mixture of anionic detergents, combined with a continuous filtration with a polypropylene filter medium; four pickling tanks for steel pickling only; two static rinse tank; de-zincing tank; flux tank; drying furnace; zinc tank; quenching tank.

Before, the firm used to buy 150 tons of hydrochloric acid per year. Our calculations showed that this acid consumption could be reduced by 50 %.

The moment at which the acid was dumped in a pickling tank was determined by its zinc contents, as the company had a buyer for the spent acid who demanded a very low zinc content. Zinc was found in significant amounts in all the pickling tanks, because the operators were not careful when selecting a tank for de-zincing defective parts and racks. So a clear separation of pickling and de-zincing became the main goal of the project.

The main weak point was the analytics used to determine the concentration of iron and zinc in the pickling baths. The operators used a graphic procedure based on the density and pH of the samples. This method was unable to differentiate between zinc and iron. Hence, photometric methods were tested for practical application in the company. They also failed, because of the mutual interference between zinc and iron, and between bivalent and trivalent iron ions. A procedure to prepare the samples by extraction was developed in the laboratory. Its implementation in daily practice, however, proved infeasible.

Only analysis by atomic absorption yielded accurate and reliable results. However, sending daily or weekly samples to an external laboratory means a large expenditure for a small company.

In the present situation, the concentration in the tanks is analysed by an external laboratory once a month. The results of these analyses are used to calculate and carefully control the volumes of acids to be topped, so the concentrations of iron and acid are kept within an optimum range.

Today, the de-zincing and pickling processes are scrupulously separated. One acid tank is used exclusively to de-zinc parts for reprocessing and racks. This acid is sold to a company that recovers the zinc from the solution. The separation allows the zinc concentration in the pickling tanks to be kept very low, allowing for a very long useful life of these acids.

As a first result, the specific consumption of hydrochloric acid during the first six month of 2004 was reduced by more than 50 %. The spent acids were completely separated into a fraction rich in zinc and one practically free of zinc. Both fractions are sold as by-products. The zinc-free acid is used in the production of wastewater treatment chemicals.

Rotoform GmbH

Rotoform produces printing cylinders for the graphics industry, and has 20 employees. The firm uses a new standard galvanic line to process the cylinders. After the copper plating or chromium plating, the cylinders run through a surface-processing machine.

The wastewater from the galvanic plants is separated into alkaline and acid flows, then collected and detoxified in a neutralisation plant. A batch treatment is used to reduce the chromium and precipitate the metals. A filter press and an ion exchanger are also used in this process.

The finished cylinders are delivered to printers.

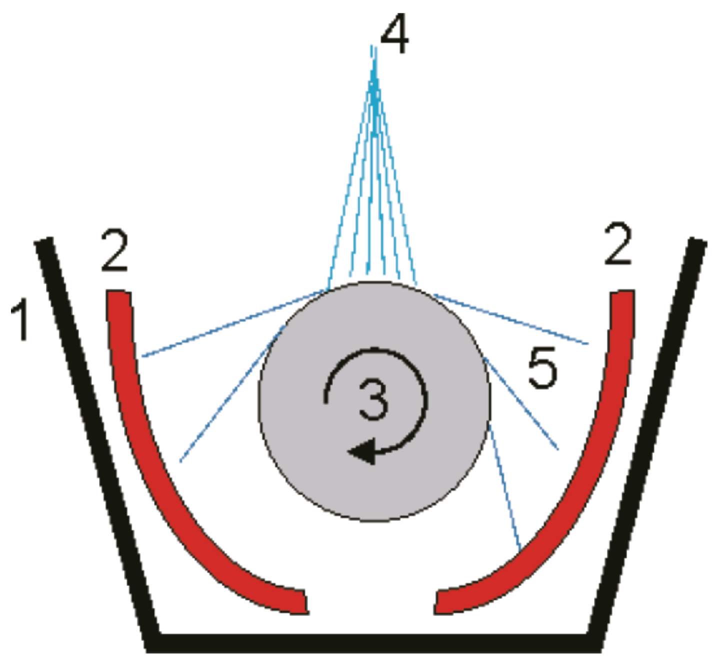

Figure 7.6 Rinsing process in the copper baths. 1. Container of the copper bath; 2. Copper electrode; 3. Rotating pressure cylinder; 4. Spray fog; 5. Water spray on the copper electrodes

The problematic materials in the production of printing cylinders are copper, chromium and nickel. The chromium cycle is largely closed, and the small amount of chromium VI that is lost through the exhaust system is reduced entirely to chromium III in the neutralisation plant.

Via the nickel and copper baths, the respective sulfates enter the neutralisation and wastewater treatment plant. Since it is difficult to break down sulfate, the company is searching for a way to reduce the sulfate contents of the wastewater. The amount of rinsing water per print cylinder was calculated, using equations from the literature to calculate the water consumption of the spray-rinses.

The reason, why significantly larger volumes of water were consumed than theoretically necessary, was the inappropriate geometry of the nozzles and the high water pressure (Figure 7.6), which meant that not only the surfaces of the copper cylinders were sprayed, but a significant portion of the rinsing water was deflected from the surface and rinsed acid from the electrode cage. This effect was minimised by using special flat nozzles and reducing the water pressure. After some test trials with a supplier, an appropriate type of nozzle was found, and was retrofitted in all copper plating machines.

The results were: a reduction of the water consumption of the plant by 40 %, a reduction of the acid dragout by 30 %, and a production increase by 25 %. A further reduction of the consumption of water and acid by 80 % seems feasible in the future.

7.8 Conclusions

The ZERMEG method was applied to five galvanic plants with different processes (wire production, printed circuit board production, hot-dip galvanising, anodising and the production of printing cylinders). The results are very promising.

The rinsing technology used by the wire producer was changed by the following measures: the combination of a two-stage rinsing cascade with a static tank to form a three-stage rinsing cascade and the separation of the rinses in the continuous pickling plants into three-stage rinsing cascades.

The volume of rinsing water in the static pickling has already been reduced by 50 %. At the same time, a theoretical approach that should allow the spent acids to be used in another company has been developed in recent months.

Two improvements were implemented at the printed circuit board manufacturer's: an electrolysis plant to recover copper from etching concentrates and rinsing water; and the use of caustic stripping solutions to neutralise acid concentrates.

This company was able to acquire a practically new used electrolysis plant. The feasibility study showed that the plant should definitely be installed. Because of capacity issues, however, the electrolysis plant was not installed at the location which participated in the project, but at a sister plant, which now recycles 20 kg of copper from the wastewater each day. The wastewater treatment plant now uses caustic concentrates after filtration to neutralise acidic concentrates. This saves 20 tons of caustic soda and a similar volume of hydrochloric acid a year.

At the hot-dip zincing plant, a consistently separated management of pickling tanks was introduced by completely separating the de-zincing and pickling operations. They are currently recycled completely by two other companies. The topping up of the pickling baths is done on the basis of monthly bath analyses and consistent application of the mixing rules. This has reduced the acid consumption in 2004 by 50 % compared to 2003.

In the anodising company, the direct evaporation of the rinsing water offered a good opportunity to install a complete rinsing water cycle. No organic compounds were found in the distillate, and its salts content is very low. This process should be implemented, if there is enough space for a third stage in the two rinsing cascades.

At the printing cylinder manufacturer, the galvanising machines were equipped with new flat nozzles with an optimised geometry, and water pressure was minimised. This reduced the water consumption by 50 % and the acid consumption by 40 %.

We have shown shown that it is feasible to approach the goal of an (almost) zero waste galvanising industry. Important steps towards the realisation of the concept were achieved in the case studies (Table 7.4) by implementing good housekeeping options and simple technology transfer. The implementations included measures which pay back in 0.5–3 years. Additional measures to further decrease the disposal of acids and caustics to the wastewater are technically feasible, but remain too expensive.

The effect of the implemented measures on the environmental impact was assessed using the MIPS model (Material intensity per service unit, www.wuppertalinstitut.de). This model uses standard data to calculate the total resource consumption caused by different materials, including biotic and abiotic resources, water and air. The standard consumption rates, used here for acids, caustic and copper, are given in Table 7.5. The prices used for the evaluation are given in Table 7.6. These prices vary greatly, depending on lot size, availability and local conditions. Table 7.7 presents the results of the environmental and financial evaluations.

The measures at Pengg were implemented to improve the management of the wastewater treatment plant, which is easier at lower hydraulic loads.

Table 7.4 Summary of the ZERMEG results

Company	Reduction of specific water consumption	Reduction of specific consumption of pickling medium (acid, caustic soda)	Other
Anodisieranstalt Heuberger	95 %	50 %	
AT&S	--- [a]	--- [b]	Recovery of 20 kg/d copper, savings of 20 tons/yr of caustic soda, external use of sludge
Joh. Pengg AG	50 %	--- [c]	Complete external use of spent acids planned
Mosdorfer GmbH	--- [b]	50 %	Complete external use of spent acids achieved
Rotoform GmbH	40 %	50 %	

[a] not relevant, because only the wastewater treatment was analysed
[b] no wastewater from rinsing, because rinses are used completely to make up pickling baths
[c] not yet analysed

Table 7.5 Standard MIPS for acids, caustic and copper

Material	MIPS abiotic materials	MIPS water	MIPS air
Copper	179.0	236.0	1.0
Sulfuric acid	0.3	4.0	0.7
Hydrochloric acid	3.0	40.0	0.4
Caustic soda	3.0	90.0	1.0

Table 7.6 Standard prices for chemicals

Material	[€/t]
Copper	3,700
Sulfuric acid	150
Hydrochloric acid	300
Caustic soda	300

Table 7.7 Evaluation of the measures

	Savings		Savings [kg/yr]			Total	Sav-ings	Pay back
Comp	Cate-gory	Total amount	Abiotic MIPS	water MIPS	air MIPS	MIPS	[€]	
Heu-berger	Water	57,000 m³/yr		57,000,000		57,000,000	57,000	<3 years
	Caustic soda	5000 kg/yr	15,000	450,000	5000	470,000	1500	<3 years
AT&S	Copper	4400 kg/yr	787,600	1,038,400	4400	1,830,400	16,280	<2 years
	Caustic soda	20,000 kg/yr	60,000	1,800,000	20,000	1,880,000	6000	<1 year
Pengg	Water	17,600 m³/yr	---	17,600,000	---	17,600,000	---	---
Mos-dorfer	Hydro-chloric acid	75 t/yr	225,000	3,000,000	30,000	3,255,000	22,500	<1 year
Roto-form	Sulfuric acid	50 % (approx.; investment not to be disclosed)						<1 year

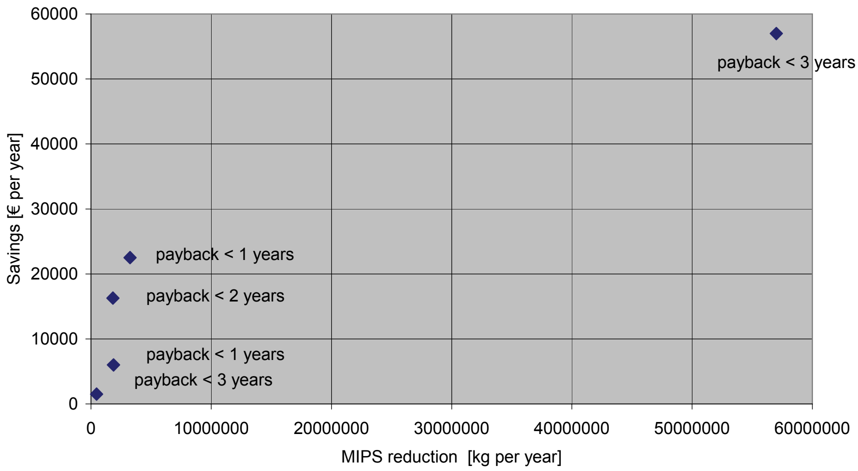

Figure 7.7 Correlation between environmental and financial savings for the measures introduced in the case studies

Figure 7.7 shows a graphic representation of the correlation between the environmental and financial savings for the measures implemented in the case studies. The correlation is positive: the higher the financial savings, the greater the reduction of environmental impact, expressed as total MIPS in kg per year.

The ratio between cost saving and environmental improvement was very similar for most technical improvement options, with one exception. This exception concerned the installation of a cooling plant to reduce the once-through use of cooling water. This improvement alone is achieving an environmental improvement that is nearly ten times larger than that of the other measures together, while the total savings from these options together would be around the same as that from this single superior option. This is due to the huge amount of well water which was previously used at a temperature of 12 °C for direct cooling because of the low temperature required in the galvanising bath (18 °C).

It is concluded that it is possible to achieve a significant reduction in the consumption of water and chemicals and at the same time reduce the generation of sludge to landfill from wastewater treatment, by employing economically favourable measures. This had not been recognised by the companies before the ZERMEG approach was applied. For the range of improvement arrived at during this project, economic and ecological objectives actually converged.

If measures with a pay-back time of more than 3 years have to be implemented, subsidies are needed to reduce the risk for the investor. In view of the present economic conditions, in terms of water and energy prices, this is relevant for most technologies to recycle process baths internally (such as membrane technologies and evaporators).

To disseminate the ZERMEG approach, benchmarks from these applications, documents on the demonstration projects, a manual and a programme for self-analysis of interested companies were made publicly available on www.zermeg.net. This homepage was accessed by 8,500 users in 2004.

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