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Practical experiences with the implementation of the concept of zero emissions in the surface treatment industry in Austria

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Abstract

The authors have developed the approach of the “Zero emission retrofitting method for existing galvanizing plants” (ZERMEG). The goal of this approach is to take existing galvanizing plants as far as possible towards zero emissions. The development was supported by the Austrian ministry for science and technology within the programme “Factory of the Future”. The method consists first of an analytical step to describe the existing performance of the plant in terms of production, water input and input of chemicals, a second step is designed to characterize the theoretically possible minimum consumption using the present equipment and the third step is the comparison of the present to the ideal situation to identify optimisation options (improved draining, dosage of chemicals, control of rinsing water, mixing in the tanks, etc.).

To facilitate the calculations, a Microsoft-Excel-programme was developed (Zero Emission Program Analysis, ZEPR), which allows to calculate the ideal water consumption of different configurations of rinses, drag out for different shapes and surface conditions of parts, and changes in concentrations of active baths. A technology data bank was developed that includes information on different technologies to enlarge the useful time of galvanizing baths or to recycle spent solutions and rinsing water.

This paper describes case studies in five galvanizing plants. The measures which were implemented include changing the rinsing cascades in three plants at the wire producer Peng (reduction of the water consumption in the batch pickling plant by 50%), the use of spent caustics to preneutralise spent process baths and the implementation of an electrolysis plant to recover copper at the printed circuit board manufacturer AT&S (recovery of 20 kg/day of copper), optimising the pickling baths of the hot dip galvanizer Mosdorfer (50% reduction of consumption of acids) and the optimisation of the spray rinses in the automatic copper plating plants of the producer of printing cylinders Rotoform (reduction of water consumption by 50%, reduction of acid consumption by 40%).

The work showed, that in three of the five plants it was possible to fully avoid the discharge of spent process baths. One plant now operates at zero emissions. In one plant it would be technically feasible to do so, however, it is not economically feasible, at this time.

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Keywords: Galvanizing plants; Zero emissions; Cleaner production; Systematic approach

1. Introduction

1.1. The surface treatment industry in Europe: importance and environmental aspects

There are more than 10,000 firms in the surface treatment industry in Europe using electrolyte or chemical processes...
and about an additional 8300 companies using so-called in
house galvanic surface treatment equipment. There are about
440,000 employees in Europe working in these businesses.
The production of printed circuit boards is included in these
numbers.
Monetary loss of steel parts due to corrosion is estimated to
be 7,300,000 € annually or approximately 0.5 €/day per cit-
izen of the European Union. In light of the fact that in a mod-
ern car there are about 2000–3000 galvanised parts, and that
in an airbus there are approximately 2 million parts, the impor-
tance of the galvanizing industry becomes obvious.
The galvanizing industry also has many negative aspects.
The most obvious are a very high consumption of water,
raw materials, energy and the generation of toxic wastewater
and sludge. Approximately 1% of the hazardous waste in
Europe is produced by the electroplating industry. German re-
searchers estimated the amount of sludge from galvanizing
plants in 2002 to be 80,000 tons. For Austria, 4000 tons in
2003. Older estimations in 1997 stated numbers such as
250,000 tons of sludge, not including the wastes from anodis-
ing (about 50,000 tons) and pickling companies. Approximi-
tately 30% of the sludge is used as secondary raw material,
the remainder is currently landfilled.
Water consumption is very high in the electroplating indus-
try. Concrete numbers have been found for Germany’s anodis-
ing companies. The wastewater discharge from these
anodising companies is about 1 million m³ per year [1–3].

2. Features of common surface treatment processes

A galvanizing process can be divided into the following
steps: pre-treatment (degreasing, pickling), the plating process
and rinsing [5–7].

2.1. Pre-treatment

The surface of the components that are to be galvanised is
contaminated with organic pollutants, such as oil and grease,
or metal-oxides from the earlier production process steps.
The organic pollutants result from cooling lubricants or anti-
corrosion oils. Metal-oxides are the result of corrosion of
pure metal surfaces after contact with air. All these pollutants
have an impact on the quality of the galvanizing processes and
must be removed prior to galvanisation.

2.1.1. Degreasing

Oil and grease have a negative impact on the efficiency of
the following process steps, because the organic components
stick to metal surfaces and disable the effect of the process
chemicals. So the first process step in most plating plants is
the removal of oil and grease. Most common processes for
such degreasing are either aqueous or solvent degreasing.
In aqueous degreasing usually alkaline or neutral solutions
are used. The main constituents of degreasing solutions are
cauistics, silicates, phosphates and complexating and surface
tension reducing agents, i.e. tensides. The solution can work
as either stable emulsions or demulsifying system.

Solvant degreasing uses the efficiency and universal appli-
cability of different organic solvents. Most common are clo-
ринated hydrocarbons for special applications, which are used
in closed systems that include distillation and reuse of the sol-
vents. Typically, solvent degreasing today in Europe is used
only in special applications (e.g. very small parts with very
high quality requirements).

2.1.2. Pickling, etching and descaling

During the pickling and descaling processes oxide-layers
and scales are removed by a chemical reaction of the surface
and the pickling solution. The solution usually consists of hy-
drochloric or sulphuric acid and different pickling agents. The
removed oxide layer dissolves as ions in the solution. To as-
sure the effective removal of the oxide layer the acid concen-
tration, temperature, pickling time and ion concentration in
the solution must be controlled within certain ranges. For aluminium,
caustic soda is used as a pickling agent.
The ion concentration for an effective pickling process de-
pends on the process solution and varies between 2.5% and
12%. Common conditions for pickling solutions using sulphu-
ric acid are a concentration of 25% and a temperature of
60 °C. Hydrochloric acid baths are used with concentrations
of 18–22% and a temperature range of 30–35 °C.

2.2. The plating process

During an electroplating process a metal layer is built-up on
the component to change the characteristics of its surface. The
process consists of different steps such as the dissolution of
metal ions into the electrolyte, the movement of the ions in
the electrolyte and the deposition of the metal ions on the com-
ponent. The electrolyte is necessary for closing the current cir-
cuit and the movement of the ions, and consists of acids or
bases, which differ in their concentration and combination
from process to process. Common electroplating processes
use copper, nickel, chromium, zinc, gold, silver and aluminium.
Several other processes can be at the heart of the electro-
plating plant. Most common is hot dip zining (immersing
the clean steel into a melt of zinc to form a layer of zinc on
the base metal) and phosphatizing. In phosphatizing a layer
of insoluble phosphates is formed on the metal surface using
a solution containing phosphoric acid and/or phosphates.

2.3. Rinsing

Rinsing serves mainly two objectives. The first is the reduc-
tion of contamination of a process bath by the process solution
of a preceding bath through drag out. The second goal is to
stop chemical reactions on the surface of the component.
Drag out is the result of surface structures, which hold or
scoop process liquids. It can be reduced by an optimized ar-
angement of parts on the racks, so that the process solution
can run off the surface more easily. Extending the drip times
(to approximately 10 s), using vibration of the parts, air knives
can also help to reduce drag out effectively.
3. A vision of galvanizing without wastewater and hazardous waste

Plating processes result in emissions of wastewater, which contain metals and the process chemicals in a diluted form. Physical—chemical wastewater treatment results in the formation of sludge, which is currently usually landfilled.

An ideal galvanizing plant, on the contrary, does not produce hazardous waste or wastewater. The useful life of process baths is unlimited, because impurities are separated by suitable processes continuously. Drag out is minimized, as is water use for rinsing [4].

For the retrofitting of existing surface treatment plants there are practical limitations to this approach:

- many plants are designed to process a broad variety of parts;
- usually there is a lack of space, which is especially relevant in choosing proper rinsing technologies;
- the large number of technological options for the treatment of process solutions makes the selection for a specific application difficult, even for an expert.

Numerous manuals and studies [2] were published on the reduction of water consumption of surface treatment plants and on the improved treatment of process solutions to increase their lifetime.

However, no integrated approach to systematically identify the best possible retrofit for an existing plant with the overall objective of zero emissions by optimising bath treatment, rinsing technology, and recycling simultaneously is known.

4. The optimisation approach of “zero emission retrofitting method for existing galvanizing plants” (ZERMEG)

The “zero emission retrofitting method for existing galvanizing plants” (ZERMEG)1 to approach was designed to assist in systematic optimisation of galvanizing plants by using the following elements (Table 1):

- Methodical, stepwise, integrated approach;
- Identification of the “ideal situation”, that is the minimum possible consumption of water and chemicals with the existing configuration of the plant and systematic variation of the configuration;

<table>
<thead>
<tr>
<th>No. of step</th>
<th>Description Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Analysis of the current situation; measuring the water consumption, the usage of chemicals and the sludge production.</td>
</tr>
<tr>
<td>2</td>
<td>Analysis of the current situation; identification of drag out.</td>
</tr>
<tr>
<td>3</td>
<td>Analysis of the current situation; identification of the actual rinsing criteria.</td>
</tr>
<tr>
<td>4</td>
<td>Calculation for comparison; calculating the necessary rinsing criteria and the ideal water consumption.</td>
</tr>
<tr>
<td>5</td>
<td>Calculation for comparison; calculation of the ideal consumption of chemicals.</td>
</tr>
<tr>
<td>6</td>
<td>Identification of possible external disposal and recycling options for spent process solutions.</td>
</tr>
<tr>
<td>7</td>
<td>Identification of possible recycling options.</td>
</tr>
<tr>
<td>8</td>
<td>Evaluation of the options.</td>
</tr>
<tr>
<td>9</td>
<td>Optimisation of the wastewater plant.</td>
</tr>
</tbody>
</table>

1 ZERMEG consists of the approach illustrated in Table 1. In this process the programme ZEPRA (zero emission program analysis) is used to calculate the water consumption of different arrangements of rinsing tanks. The programme routine ZEPRA was developed using Microsoft Excel® and Visual Basic®. A freeware version of ZEPRA is available from www.zermeg.net. The full programme is available from gernot.gwehenberger@tugraz.at. For the representation of currently available treatment options, a database was created [17]. The database of technological options to improve the useful life of process solutions is included in the project report “ZERMEG” which was published in German by the Austrian ministry for Innovation and Transport (Fresner [14], available for download from www.zermeg.net).
The ZERMEG approach identifies the minimum drag out, appropriate rinsing criteria, optimum useful bath time, economically feasible measures for recycling, and maximum external use of spent solutions. This sequence guarantees maximum improvements and the most effective use of resources.

Table 2 shows potential solutions which are produced by the different steps of the optimisation procedure of ZERMEG.

This sequence guarantees that the most effective measures which at the same time require the least investments and operating costs are selected first.

Cleaner production projects done by the authors have shown, that already in the phase of analyses many effective measures with little investment are found and implemented [8,10]. The internal analyses of the galvanic process improve the worker’s awareness for problems and leads to a critical reflection [11].

All in- and out-going material flows should be recorded in as detailed a manner as possible, together with the cost of water, wastewater treatment and chemicals and a chemical and toxicological characterisation of the chemicals used [9].

The following questions should be answered:

- How good is the consistency of the data?
- What are the optimal rinsing criteria?
- Where and how much rinse water is used?
- Where are the largest volumes of chemicals used in the process?
- When and why are valuable materials discharged?

In answering these questions, the data sources presented in Table 3 are useful.

From the recorded mass flows over a representative period of time, specific consumption is calculated. Therefore, the throughput of the parts has to be recorded. In order to calculate specific indicators it is necessary to record the surface area per part and the throughput of parts per unit time. Data on the surface-related consumption of water and chemicals are essential instruments for the localisation of measures to reduce consumption. Surface area can be measured from the geometric dimensions of the parts, calculated from their weight, or calculated from the electric current in electroplating processes [14].

These data are the reference for later comparisons with the “ideal situation”.

Table 2
Identify and quantify the potential options that may be derived by applying the ZERMEG method in industrial facilities

<table>
<thead>
<tr>
<th>No. of step</th>
<th>Description</th>
<th>Shows following potentials for optimisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Analysis of the current situation; measuring the water consumption and the usage of chemicals.</td>
<td>• Collect actual process data (water consumption, chemical consumption, production); • Define indicators; • Measure daily, the concentration of solutions in the process tanks; • Provide regular feedback to the operators.</td>
</tr>
<tr>
<td>2</td>
<td>Analysis of the current situation; identification and quantification of the drag out.</td>
<td>• Analyse the time drain to overcome too short drain-times and lift-out-times; • Optimise design of parts to reduce drag out; • Improve the mounting of the parts; • Improve the rack geometry and surface.</td>
</tr>
<tr>
<td>3</td>
<td>Analysis of the current situation; identification of the actual rinsing criteria.</td>
<td>• Improve quality criteria control.</td>
</tr>
<tr>
<td>4</td>
<td>Calculation for comparison; calculating the ideal water consumption on the basis of the ideal rinsing criteria.</td>
<td>• Compare with the actual water consumption; • Monitor and control reduction of the volume of water by measuring the conductivity in order to control the volume of rinse water; • Control manually, the volume of rinse water; • Improve the rinsing technologies (two-stage counterflow rinses, three-stage counterflow rinses, static rinse tank for recovery of chemicals).</td>
</tr>
<tr>
<td>5</td>
<td>Calculation for comparison; calculation of the ideal consumption of chemicals.</td>
<td>• Improve chemical analyses; • Improve the dosage of chemicals; • Minimise overpickling; • Minimise contamination by organic compounds or metals; • Reduce viscosity of baths (by reducing concentration of chemicals, and reducing impurities); • Use simple filtration technologies; • Use new technical measures in order to enlarge the useful lifetime.</td>
</tr>
<tr>
<td>6</td>
<td>Definition of possible external disposal and recycling options.</td>
<td>• Identify useful by-products and potential clients; • Improve management of chemicals so that they fulfill the requirements of potential clients.</td>
</tr>
<tr>
<td>7</td>
<td>Definition of possible recycling options.</td>
<td>• Recycle bath solutions after cleaning with processes suggested by the technology database.</td>
</tr>
<tr>
<td>8</td>
<td>Evaluation of the options.</td>
<td>• Perform payback calculations and evaluation of sustainability of the various alternatives.</td>
</tr>
<tr>
<td>9</td>
<td>Optimisation of the wastewater plant.</td>
<td></td>
</tr>
</tbody>
</table>
The ideal water consumption is then the minimum of the water and the rinse criteria are determined as defined in Table 4.

The minimum drag out calculated according to Kimmerl [15] rinsing tanks in the plant. The input for this calculation is ing cascades of Nagy [16] for the feasible configuration of tank, spray rinse, and two- and three-step countercurrent rins-

Surface-related data about consumption and the concen-
trations of chemicals are important indicators upon which opti-
misation approaches may be built. On the one hand they are
basic information for the daily control of the system and on
the other hand they are basics for the analysis of problems
and for seeking and evaluating options for improvement [13].

The actual losses due to drag out can be identified by tests
in the company. Therefore, a certain number of products or
racks are rinsed in a rinsing tank, under the usual conditions,
and the rinse water is analysed before and afterwards.

The ideal drag out for a given geometry is calculated ac-
cording to the method of Kimmerl [15]. There will always
be a variation in the parts to be coated, the drag out must be
calculated for the different parts individually and then inte-
grated according to the surface contribution of the individual
parts.

The rinse criteria are defined as the ratio of the concentra-
tion of salts in the active baths over the concentration of salts
in the respective final rinsing water. The actual rinse criteria
are determined from measurements of the concentration of
salts in the dragged out solution and the final concentration
of the same salts in the last rinsing step in the plant.

To determine the ideal rinse criteria, the suppliers of the
chemicals used in the baths are asked for the optimum concen-
tration of the adhering liquid film on the workpieces after the
last rinse step before the respective bath. Alternatively, data
from Table 4 are used. (This table was taken from the compi-
lation of rinse criteria in [14].)

The ideal water consumption is calculated using the compi-
lation of formulae for the water consumption of a static rinsing
tank, spray rinse, and two- and three-step countercurrent rins-
ing cascades of Nagy [16] for the feasible configuration of
rinsing tanks in the plant. The input for this calculation is
the minimum drag out calculated according to Kimmerl [15]
and the rinse criteria are determined as defined in Table 4.

The ideal water consumption is then the minimum of the water

<table>
<thead>
<tr>
<th>Process</th>
<th>Required rinse criteria [14] in surface treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degreasing (in hot dip galvanizing)</td>
<td>35–100</td>
</tr>
<tr>
<td>Electrolytic degreasing</td>
<td>100–200</td>
</tr>
<tr>
<td>Pickling</td>
<td>100–200</td>
</tr>
<tr>
<td>Pickling of aluminum</td>
<td>500–1000</td>
</tr>
<tr>
<td>Anodising</td>
<td>2000–4000</td>
</tr>
<tr>
<td>Copper plating, zincing, tin plating</td>
<td>1000–5000</td>
</tr>
<tr>
<td>Burnishing, phosphating, chromating</td>
<td>2000–5000</td>
</tr>
<tr>
<td>Nickel plating</td>
<td>3000–10,000</td>
</tr>
<tr>
<td>Chrome plating</td>
<td>10,000–100,000</td>
</tr>
<tr>
<td>Electrolytic pickling and polishing</td>
<td>100,000–1,000,000</td>
</tr>
</tbody>
</table>

These numbers characterize the necessary dilution to the adhering film on the parts leaving different galvanic processes to stop the reaction or to prevent interference with the consecutive treatment.

The effect of the options is modelled by using the
programme routine ZEPRA. As the cost of water, water treat-
ment, and for chemicals is known for the present configura-
tion, it now can be compared to the potential cost after the
relevant changes. This procedure is quite new. No known
cleaner production manual for surface treatment includes
this mathematical formulation of the minimum possible water
consumption on the basis of the necessary rinsing criteria
(review of 700 manuals and fact sheets for cleaner production
in Refs. [18–20]).

The following process steps are currently represented in
ZEPRA:

- Pickling;
- Degreasing;
- Anodising;
- Evaporation;
- Drag out;
- Rinsing.

For each of these parameters a template is developed in
which the calculation of the output streams is done from the

<table>
<thead>
<tr>
<th>Data source</th>
<th>Calculation of water from the accounting department records.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals</td>
<td>Accounting department records.</td>
</tr>
</tbody>
</table>

The evaluation of the current situation should lead to the
following results:

- Transparency of the whole galvanic process including the
wastewater treatment in terms of the existing materials
flows and their relevance of waste minimization options;
- Identification of the main sources of relevant material
losses;
- Identification of the processes with a high demand for
rinsing;
- Identification of the process baths with a high dumping
frequency.

The ideal water consumption is calculated using the compi-
lation of water from the accounting department records.

The rinse criteria are defined as the ratio of the concentra-
tion of salts in the last rinsing step in the plant. The input for
this mathematical formulation of the minimum possible water
consumption of the feasible configurations of rinsing tanks in-
cluding the addition of rinsing stages, depending on space and

The ideal consumption of chemicals in the active baths is
calculated from the ideal minimum drag outs and the models
for the chemical reactions being used in the process.

These results are the starting point in selecting options.
Knowing the ideal final result for the feasible configuration of
the plant, clear priorities for improvement measures can be
identified from Table 2 (third column) according to the rele-
vance of their contribution to approach the ideal final result.
The further optimisation then consists of the identification of
alternatives to the rinsing system, selecting appropriate treat-
ment technologies and selecting appropriate recycling

These steps include the identification of the alternative
configurations of the plating plant (additional rinse tanks, in-
troduction of membrane units, ion exchangers, filters, evapora-
tors, etc.).

The effect of the options is modelled by using the
programme routine ZEPRA. As the cost of water, water treat-
ment, and for chemicals is known for the present configura-
tion, it now can be compared to the potential cost after the
relevant changes. This procedure is quite new. No known
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ZEPRA:

- Pickling;
- Degreasing;
- Anodising;
- Evaporation;
- Drag out;
- Rinsing.

For each of these parameters a template is developed in
which the calculation of the output streams is done from the
input streams and from all additional necessary parameters. Each bath and each separation operation is treated as a black-box. This allows the researchers/operators to easily add new models for baths and recycling operations.

ZEPRA calculates, step by step from the input data the drag out, evaporation losses, concentration changes, consumption of chemicals and water consumption of a given sequence of galvanic baths.

After the identification of the ideal drag out and rinsing criteria, already a number of options can be given (Table 2).

For the representation of currently available treatment options, a database was created [17]. It is based on technologies available 2002. It lists

- technologies;
- description of the working principle of the technologies;
- qualitative and quantitative characterisation of inputs, outputs and by-products;
- investment and operation costs.

5. Case studies

The method of ZERMEG was applied to five surface treatment enterprises with different processes: anodising [1], printed circuit board production (AT&S), wire production (Pengg AG), production of printing cylinders (Rotoform), and hot dip galvanizing (Mosdorfer).

Table 5 shows the results of the case studies in terms of reduction of specific water consumption (water consumption per square meter of surface or product or per ton of product) reduction of consumption of pickling media, and the future potential. Table 5 illustrates the economic effects in terms of savings both in physical and monetary units, and payback.

<table>
<thead>
<tr>
<th>Company</th>
<th>Reduction of specific water consumption</th>
<th>Reduction of specific consumption of pickling medium (acid, caustic soda)</th>
<th>Other improvements</th>
<th>Future potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodisieranstalt</td>
<td>96%</td>
<td>50%</td>
<td></td>
<td>Zero wastewater by installing three-stage rinsing cascades and evaporator for rinsing water recovery.</td>
</tr>
<tr>
<td>Heuberger</td>
<td>b</td>
<td>a</td>
<td>Recovery of 20 kg/day copper, savings of 20 tons/year of caustic soda, external use of sludge.</td>
<td>Additional 30% reduction of rinse water.</td>
</tr>
<tr>
<td>AT&amp;S</td>
<td></td>
<td></td>
<td>Complete external use of spent acids.</td>
<td>Additional 40% reduction of rinse water.</td>
</tr>
<tr>
<td>Joh. Pengg AG</td>
<td>50%</td>
<td>c</td>
<td>Complete external use of spent acids realized.</td>
<td></td>
</tr>
<tr>
<td>Mosdorfer GmbH</td>
<td>d</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotoform GmbH</td>
<td>40%</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a ZERMEG consists of the approach illustrated in Table 1. In this process the programme ZEPRA (zero emission program analysis) is used to calculate the water consumption of different arrangements of rinsing tanks. The programme routine ZEPRA was developed using Microsoft Excel® and Visual Basic®. A freeware version of ZEPRA is available from www.zermeg.net. The full programme is available from gernot.gwehenberger@tugraz.at. For the representation of currently available treatment options, a database was created [17]. The database of technological options to improve the useful life of process solutions is included in the project report "ZERMEG" which was published in German by the Austrian ministry for Innovation and Transport (Fresner [14], available for download from www.zermeg.net).

b Not relevant, because only the wastewater treatment was analysed.

c Not yet analysed.

d No wastewater from rinsing, because rinses are used as makeup for pickling baths completely.

In all the companies, the approach of documenting the actual water consumption, the actual and minimum drag out, the identification of the necessary rinse criteria and the identification of the optimum rinsing system provided an effective starting point for significant improvements in terms of water consumption and reductions in use of chemicals. In the following paragraphs these case studies are described in details.

5.1. Anodisieranstalt Heuberger

This company with its 24 employees is a typical Austrian SME. The number of employees has increased from 15 to 24 in the last years as production increased from 20,000 to 96,000 m²/year.

The company anodises aluminium surfaces. In this process the aluminium surface is converted to an oxide film. It protects the anodised aluminium to a large extent from corrosion and abrasion. The enterprise works on parts of diverse shapes and sizes. The spectrum covers profiles for fassades, windows and solar panels and sheet metals as well as small articles such as parts for transmissions and engines, exhaust systems, parts for bicycles, parts for mechanical engineering and parts for the medical technology.

During this work the average grease and oil film of the material coming from the customers, was determined. It was documented that polished parts are practically grease and oil-free, while mechanically treated parts and sheet metal had an average oil rate of approximately 1 g/m² surface.

After degreasing in a light alkaline bath the parts are pickled in caustic soda solution. Thus, a metallic surface is produced. 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 workpieces, in order to avoid uneven pickling of the 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. This results in a relatively large drag out of pickling solution to the subsequent rinse tanks.

The drag out was subject to intense investigations. It was shown that after the pickling the drag out was several times higher than expected by the operators.

After rinsing, the aluminium parts are immersed in an electrolyte of sulphuric acid. By applying an electric current an oxide coating is produced.

After anodising, the parts are again rinsed. As a final step they are treated in a steam vapor atmosphere containing acetic acid in a covered tank.

Thereafter, the parts are examined for their technical and decorative quality. Then the finished parts are carefully packed.

In the enterprise, detailed records were introduced which document on a daily basis:

- Water consumption;
- Energy consumption;
- Measurements of bath concentrations;
- Addition of chemicals;
- Discharge of baths;
- Special observations.

These data are discussed by the manager and the operators every day in the morning meeting.

The surface area of the parts which are processed were calculated daily from the current in the anodising tank, which is proportional to the surface area of the parts, which act as anode. A typical current is 1.5 A/dm². The current was controlled automatically. The surface area was calculated by the control programme of the rectifier and documented.

By this the following weak points were identified:

The actual drag out, particularly after pickling, was higher than the theoretical amount. On the one hand the drag out was very high because of the high viscosity of the pickling solution. On the other hand a large number of parts were reprocessed after errors in the galvanic treatment. By employing good housekeeping measures (increased control of the bath conditions to their optimum range (temperature and chemical concentrations) to lower viscosity; improvement of the work instructions and control of the effective implementation of the work instructions to minimize errors) a significant reduction of drag out and of the error rate from 4% to less than 2% of parts was achieved. A target of less than 1% mistakes seem not realistic considering the broad variation of parts, clients and the manual handling.

With the existing rinsing configuration of one, two-stage rinse cascade after pickling and one after anodising, the amount of rinse water used to achieve the desired rinsing criteria, was much higher than theoretically necessary (compared to best practise, which is a three-stage rinse cascade). By concentration measurements in the rinses it was found that due to the high viscosity and density of the media and the poorly functioning circulation of the rinses (through compressed air) a pronounced concentration gradient from top to bottom of the rinse tank existed in the rinses. By stronger bath circulation with compressed air and the introduction of a constant circulation during production stops by keeping the air on, a more uniform concentration was obtained.

In the anodising baths, a significantly increased consumption of sulphuric acid was documented compared with ideal consumption. The retardation plant for the extraction of dissolved aluminium was identified as the cause. The retardation plant is based on the principle of the different surface absorption of sulphuric acid and aluminium on a resin. This resin was very old at the beginning of the work. After it was replaced, a clear improvement of the performance of the plant was achieved, which led to a clearly reduced acid discharge. Through these two measures it was possible to reduce sulphuric acid usage by more than 30%. The quantities of water evaporated were calculated depending on the temperature and air speeds in the hall. It was shown that with the quantities of water used, evaporation from the baths contributes only a small part to the total water consumption.

It was found that the actual water consumption was determined by the cooling water needed to keep the temperature in the anodising tank at 18 °C, which is the optimum temperature. This water was used as rinse water. In order to reduce the huge quantities of cooling water used to keep the temperature of the anodising baths within the required range, a closed cooling cycle with integrated refrigerators was designed and installed. Due to this measure the quantity of cooling water was decoupled from the amount of rinse water. Thus, an adjustable, controlled amount of rinse water was achieved.

Before, quality problems almost automatically were associated with rinsing problems. Now errors are documented and classified into the following categories:

- Problems induced by the suppliers of the materials (defects in the surface, wrong declaration of desired treatment);
- Errors with the mechanical pre-treatment, such as bad finishing or polishing;
- Pickling and rinsing errors, such as overpickling or stains from bad rinsing.

Out of this classification, appropriate strategies for their prevention are developed. Previously the first response to any quality problems always had been to increase the water flow in rinsing. This knowledge served as the basis for additional training activities in the enterprise and for installation of automated water flow through the rinses.

Meanwhile the total specific water consumption (rinse water consumption per square meter of surface of product
processed) was reduced to less than 4% of the initial volume. Originally the consumption was 20,000 m$^3$ with a processed surface area of 16,000. Now, because of better organisation and better workflow they are processing 96,000 m$^2$ with a water consumption of less than 5000 m$^3$.

The results of the water use optimisation at Anodisieranstalt Heuberger are shown in Fig. 1.

The necessary investment for the closed cycle cooling plant (investment 60,000 €), renovation of the retardation plant, spray rinses, new rectifier allowing better control, new programme for the crane, training for the operators, was 100,000 €. The savings from the reduction in water consumption was calculated to be 57,000 €/year based on actual production.

Zero emission operation in this plant regarding wastewater is feasible by upgrading the two-stage rinse cascades to three-stage ones, and recovering the final rinse water by evaporation. Tests to do so were successful, however, at present this solution is economically not viable, as there is no space for the third rinse stage within this facility, as the production area is already fully occupied and the neighbour is not willing to sell land to the company.

Ideally, the plant should have a cascade of three rinses after the pickling and the anodising tank, both linked to an evaporator to recycle the water of each rinse phase of the cascade. This would cost approximately 150,000 € investment, saving approximately 5000 € in water and wastewater treatment. However, this is not feasible, because the space for the rinses is not there unless the neighbouring lot could be acquired.

5.2. AT&S

AT&S produces printed circuit boards for cars and mobile phones. The work presented here was done in their plant in Fohnsdorf in Austria, where they employ 200 people. Following the suggestion of management, the focus of the study was not the actual production, but the effluents of the etching lines.

In the production of printed circuit boards, first the desired pattern is masked by printing it with a special lacquer on the copper layer on the board. Then the parts, which are not covered, are etched. After rinsing the boards are activated in baths using sodium persulphate are used to clean the surfaces to allow easy soldering of electronic components. Then the boards can be drilled, punched and sheared.

During the etching of printed circuit boards, copper containing concentrates (up to 40 g/l) and rinse water are generated. Depending on the process between 0.5 and 2 μm of copper are dissolved. This copper was precipitated in the wastewater treatment plant in the past.

Because the process solutions were changed frequently in this plant, the optimisation of the use of the concentrated process solutions was the focus of the project. Two options were identified:

- electrolysis to recover copper from effluents before discharging them to conventional wastewater treatment;
- use of caustic stripping solutions for the partial neutralisation of acidic concentrates.

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 that can be recycled. At the same time the amount of persulphate use is reduced. The benefits of electrolysis are as follows:

- minimization of hydroxide sludge;
- saving of the reducing agent;
- recovery of copper.

A drum electrolysis cell was selected for copper recovery. In this cell copper balls rotate, onto which the copper from the wastewater is precipitated. The concentration of residual copper after treatment in the cell is as low as 0.5—1.5 g/l. This is removed then in the physical chemical wastewater treatment plant. The benefits of the drum electrolysis cell are good hydrodynamic properties and a high electrical efficiency up to 70% (Table 6).

If a new plant had to be bought, however, the project would not have been feasible. Because of the shut down of another plant, a used, but however practically new electrolysis plant with matching capacity could be acquired. The revenue from the recovered copper and the savings of wastewater treatment chemicals and the reduced sludge for disposal resulted in a payback time of 15 months.

The strongly caustic stripping solutions were cleaned in the past by filters and an ultrafiltration plant before neutralising them with hydrochloric acid. Now the caustic concentrates are used for the partial neutralisation of acidic concentrates in the wastewater treatment plant. So annually approximately 20 tons of caustic soda and a similar quantity of hydrochloric acid can be saved.

5.3. Joh. Pengg AG

Joh. Pengg AG is specialized in the production of wires for sophisticated applications in the automobile, electrical and
machine manufacturing industries. These products have to have very precise dimensions. High requirements exist regarding the mechanical parameters of these wires. The company is certified according to VDA 6.1, ISO 9001, and QS 9000. The plant employs 250 people.

Production of the wires is done in several steps. Among these steps, three are surface treatment steps. These three (batch pickling plant and two continuous pickling plants) were analysed in this project.

Initially, wire rod is pickled in a batch plant using hydrochloric acid. After pickling it is rinsed in a two-step rinse cascade using cold water. The next rinse is with water at 45 °C, followed by phosphatizing and rinsing again in the same hot water tank. After drying and drawing, the wires are heat treated, followed by continuous pickling and phosphatizing in two plants, depending on the dimension of the final product. Calculations as described above showed a reduction potential in rinse water of up to 80% in the static pickling stage, by changing the configuration of the rinsing tanks, by combining the two-stage rinse cascade with the static hot water rinse tank to a three-stage rinse cascade. This change was implemented.

Practically, measurements after setting up the new layout showed, that the volume of rinse water in the static pickling tank could be reduced by 50%. This was less than the expected 80%. The reasons were shortcuts in the water flow on the floors of the tanks which could not be fully avoided because of the location of the connecting pipes. As a next step, the separation of the rinses in the continuous pickling plants into three-stage rinse cascades is currently being implemented. Again a reduction of water consumption for rinsing by 80% is expected.

Currently, the plant does not dispose of spent acids any more, as they are used as raw materials by another company. Future work is planned to fully realise the potential to reduce the quantity of rinse water.

5.4. Mosdorfer GmbH

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

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

The following baths are used in the zining plant:
1. degreasing at a pH of 8–9, and 60 °C with a mixture of anionic detergents, to which a continuous filtration is performed with a poly propylene filter medium;
2. four pickling tanks for steel pickling;
3. two static rinse tanks;
4. a dezincing tank;
5. a flux tank;
6. a drying furnace;
7. a zinc tank;
8. a quenching tank.

Prior to our work with them, they purchased 150 tons of hydrochloric acid annually. From the calculations with ZEPPRA, applying the calculated drag out and the ideal rinse criteria we concluded, that the consumption of acid could be reduced by 50%. This goal could be reached in this case study.

The useful lifetime of the acid in the picklings tank was limited by the concentration of zinc. Because the company had a client for the spent acid, who demanded a low concentration of zinc, and the zinc was present in significant concentrations in all the pickling tanks, because the operators were not careful when selecting a tank for dezincing defective parts and racks, clear separation of the pickling and dezincing processes became the main goal of the project.

The main weak point was the analytical processes used to determine the concentration of iron and zinc in the pickling baths. The operators used a graphic procedure on the basis

<table>
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<th>Company</th>
<th>Savings category</th>
<th>Total amount</th>
<th>Annual savings (€)</th>
<th>Payback</th>
<th>Comment</th>
</tr>
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<tr>
<td>Heuberger</td>
<td>Water</td>
<td>57,000 m³/yr</td>
<td>57,000</td>
<td>&lt;2 yrs</td>
<td>City water, fivefold production increase over project time</td>
</tr>
<tr>
<td>AT&amp;S</td>
<td>Caustic soda</td>
<td>5000 kg/yr</td>
<td>1500</td>
<td>&lt;3 yrs</td>
<td></td>
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<tr>
<td>Pengg</td>
<td>Caustic soda</td>
<td>4400 kg/yr</td>
<td>16,280</td>
<td>&lt;2 yrs</td>
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<td>Hydrochloric acid</td>
<td>20,000 kg/yr</td>
<td>6000</td>
<td>&lt;1 yr</td>
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</tr>
<tr>
<td>Rotoform</td>
<td>Sulphuric acid</td>
<td>15 t/yr</td>
<td>150</td>
<td>&lt;3 yrs</td>
<td>Purely organizational changes</td>
</tr>
</tbody>
</table>

Table 6
Cost/benefit analyses of the five Austrian electroplating company case studies
of density and pH of the samples. This method was not suitable to differentiate between zinc and iron. So photometric methods were tested for practical application in the company. They also failed, because of the mutual interference of zinc and iron, and of two- and trivalent iron ions. A procedure to prepare the samples by extraction was developed in laboratory scale. Its implementation in daily practise, however, proved not feasible.

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

Now, once a month, the concentration iron and zinc in the tanks is analysed by an external laboratory. On the basis of the results of these analyses, the volumes of acids to be added are calculated and carefully controlled. So the concentrations of iron, zinc and acid are kept in an optimum range.

Dezincing and pickling are now carefully separated, by consequent organisation: one acid tank is used exclusively for dezincing of parts for reprocessing and racks. This acid is sold to a company that recovers zinc from the solution. By this separation, the zinc concentration in the other pickling tanks can be kept to less than 2 g/l.

This allows for a very long useful life of these acids. When they are exhausted after 6 months, they are transferred to another company which uses them to produce wastewater treatment chemicals.

As a first result, during the first six months of 2004 the consumption of hydrochloric acid per ton of material processed could be reduced by more than 50%. The spent acids could be completely separated into a fraction rich in zinc and one practically free of zinc. Both fractions give useful by-products, when they are exhausted after 6 months.

Since the rinse water is used to prepare the pickling acids, currently the plant is operating without the generation of hazardous waste or wastewater.

5.5. Rotoform GmbH

The Rotoform company with 20 employees, produces printing cylinders for the graphic business by recycling printing cylinders. Rotoform uses a new standard, fully encapsulated galvanic-line for its production.

The old cylinders, which have to be prepared for new orders, have to be cleaned and etched first, before the surface can be reformed. The main process step then is applying a fresh layer of copper. This is done by electrodeposition of copper from a coppersulphate solution.

During the subsequent rinsing, copper and sulphate enter the wastewater treatment plant. So the company was searching for a possibility to reduce the sulphate contents in the wastewater.

The drag out of sulphuric acid was measured to be 400 g/m² of cylinder surface. The ideal minimum drag out calculated from the concentration of the electrolyte and the surface area using the formulae of Kimmerl [15] is 1 g/m².

The reason for the significantly higher amount of acid was the use of an inappropriate geometry of the nozzles and a high water pressure (Fig. 2). The rinsing water was not properly directed towards the surface of the cylinders. A significant portion of the rinse water was deflected from the surface and in the process it removed acid from the electrode cage.

This wastage was minimized by the use of special flat nozzles and a reduction of the water pressure. After some test trials with a supplier, an appropriate type of nozzle was identified. This type was retrofitted in all copper plating machines.

The results were as follows:
- Reduction of the water consumption of the plant by 40%;
- Reduction of the acid lost by 30%;
- In the same time the production was increased by 25%.

All in all, 1 ton of sulphuric acid was saved at an investment of 500 € for new nozzles. A future reduction of the consumption of water and acid by 80% seems feasible based upon the estimations of the operators after assessing the actual performance of the new nozzles after the changes.

6. Conclusions

The method of ZERMEG was applied to five surface treatment enterprises with different processes (anodising, wire
production, production of printing cylinders, hot dip galvanizing, printed circuit board production).

At the wire producer the rinsing technology was changed in the following ways:

- Replacement of a two-stage rinse cascade with a static tank to a three-stage rinse cascade;
- Separation of the rinses in the continuous pickling plants into three-stage rinse cascades.

The volume of rinse water in the static pickling phase was reduced by 50%. Parallel to these studies a practical approach was developed over the last month to use the spent acids in another company.

In the printed circuit board manufacturer, the changes that were implemented included:

a. The installation of an electrolysis plant to recover copper from etching solutions and from rinse water;
b. The use of caustic stripping solutions for the neutralisation of acid concentrates was implemented. Daily 20 kg of copper are now recovered from the wastewater. In the wastewater treatment plant, currently caustic concentrates are used after filtration to neutralise acidic effluents. This saves annually 20 tons of caustic soda and a similar volume of hydrochloric acid.

In the hot dip zincing plant consequent management of pickling tanks was introduced to separate the dezincing and the pickling completely. Now they are recycled completely by two other companies. The additions to the pickling baths are now performed on the basis of weekly bath analyses. By this the acid consumption for the year 2004 was reduced by 50% compared to 2003. The plant now operates without producing any wastewater or hazardous waste.

In the anodising company the water consumption was reduced to 4%. In this case, the installation of an evaporator to fully close the rinsing water cycles is not economically feasible presently.

At the printing cylinder manufacturer the galvanizing machines were equipped with new flat spray nozzles with an optimized geometry and the water pressure was reduced. Thus, the water consumption was reduced by 50% and the acid consumption by 40%.

All the implemented measures showed payback times in between 0.5 and 3 years.

The following fields of action for future work were identified:

- Simple, easy to use, and cheap analysis methods for determining concentrations of metals in acids and caustic process solutions;
- Collection of real experience with the operation of existing plants to enlarge the useful life of galvanic baths, especially to characterize the mechanisms of fouling and scaling;
- Testing and further developing combinations of processes to enlarge the useful life of galvanic solutions (combinations of precleaning and membranes, precleaning and ion exchangers) to take care of impurities in the practical processes (organic materials, process chemicals, and metals);
- Focused analysis of the potential to use the spent process baths externally and analyse the possibilities to create the infrastructure to collect the materials and realize the potential for reuse and recycling.

It seems feasible to approach the goal of an (almost) zero waste galvanizing industry. Important steps towards the realization of the concept were achieved in the case studies (Table 4) by analysing drag out and rinse criteria, implementing good housekeeping options and implementing already proven technology, which the companies of this study were not familiar with. The implemented changes included measures with paybacks between 0.5 and 3 years.

If measures with a payback time of more than 3 years should be implemented subsidies are needed, which reduce the risk for the investor. This includes the use of membrane technologies, and evaporators to fully recycle rinsing water given Austrian water prices (approximately 1 €/m³).

To disseminate the approach of ZERMEG, benchmarks from these applications, the documentation of 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 8500 users in 2004, and by 11,000 in 2005. There were 300 downloads of the calculation routines, and more than 5000 downloads of the report [14].

The research team plans to go back to the companies in the autumn of 2006 and document the actual consumption of water and chemicals. Present applications of ZERMEG include three more companies in Austria and six in India.

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References

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