# ECO–OPTIMIZATION OF RINSING AND RECYCLING NETWORKS IN METAL FINISHING

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Produktionsprozesse nachhaltiger zu gestalten ist ein ebenso betriebswirtschaftliches wie umweltorientiertes Ziel, das seinen Niederschlag in Kostensenkung und umweltfreundlicher Gesamtbilanz finden kann. Für Optimierungsansätze bedeutet das, dass multikriterielle Probleme gelöst werden müssen. Das sich aus dieser Forderung ableitende Ziel dieser Arbeit ist es, eine allgemein anwendbare Optimierungsmethode zu entwickeln, die einen Beitrag zum Design ökologisch und ökonomisch (*eco-eco*) „besserer" Gesamtprozesse liefern kann und in diesem Sinn ein Werkzeug für ein *Eco-Prozessdesign* darstellt.

Für den produktionsintegrierten Umweltschutz im Bereich der Oberflächentechnik sind Vorbehandlungsstraßen der Automobilproduktion besonders interessant, da sie abwasser- und chemikalienintensiv sind. Die Prozesslösungen, so genannte Elektrolyte, bestehen häufig aus wässrigen Metallsalzlösungen wie Chrom-, Kupfer-, Nickel- und Zinkverbindungen und verschiedenen Zusatzstoffen. Im Anschluss an den Behandlungsprozess sollen die Elektrolytreste, die den Werkstücken anhaften, durch eine Spülung mit Wasser (in Spülbädern/ Spülsystemen) entfernt werden.

In diesen Spülsystemen werden beträchtliche Abwassermengen erzeugt und dem entsprechend wird in größeren Mengen Wasser verbraucht. Wird das gebrauchte Spülwassers verworfen, so gelangen den aus den Prozessbädern verschleppten Stoffen als zum Teil potenzielle Wertstoffe ins Abwasser und belasten als zum Teil toxische Chemikalien (z.B. Schwermetalle) die Umwelt.

Um Nachhaltigkeit bei der Technikgestaltung von Vorbehandlungsstraßen steigern zu können, müssen vor dem Hintergrund der geforderten Produktqualität Umweltverträglichkeit und Wirtschaftlichkeit der Prozessalternativen gleichzeitig betrachtet werden. Da eine Vorbehandlungsstraße aus einer Reihe von Teilprozessen besteht (Anzahl n), die in sehr vielen verschiedenen Möglichkeiten (maximal $2^{n-1}$) verschaltet werden können, sind die Alternativen nicht mehr nach jeweils einzelner Prozessauslegung vergleichbar, denn schon bei $n = 10$ wären das bereits bis zu 1023 aufwändig zu berechnende Möglichkeiten, den Prozess zu gestalten.

Aus diesem Anlass sollte, so lautet die zentrale Aufgabenstellung der Arbeit, eine ECO-Optimierungsmethode entwickelt werden, die auf der Basis einer so genannten Superstruktur sowohl die ökologischen als auch die ökonomischen Aspekte bei der Prozesssynthese simultan berücksichtigt.

Zentrales Ergebnis ist ein Algorithmus (*Simultaneous Analysis of Environmental Impacts Sensitivity*, SAEIS), der es erlaubt, die ökologischen Aspekte zu quantifizieren und dann gemeinsam mit jährlichen Gesamtkosten (TAC) der unterschiedlichen Anlagenkonfigurationen in eine multi-kriterielle Zielfunktion zu integrieren.

Zuerst werden die Umweltauswirkungen in Form von verschiedenen Wirkungsindikatorergebnissen in Zahlen ausgedrückt. Dann muss ein repräsentativer Wert, der die Umweltrelevanz des Systems beschreibt, ermittelt werden. Weil die direkte Aggregation von Wirkungsindikatorergebnissen über Substanzen nach ISO-14000 Normen nicht erlaubt ist, wird das Maximum der Wirkungsindikatorergebnisse ausgewählt, um das größte Umweltauswirkungspotenzial des Systems darzustellen. Dieses repräsentative Maximum wird in die multi-kriterielle Zielfunktion des SAEIS-Algorithmus integriert.

Anhand von zwei Fallbeispielen von Vorbehandlungsstraßen der Automobilproduktion wurde der Algorithmus zur Optimierung des Designs von Spülsystemen implementiert. Für die Prozesssynthese von zunächst der Vernickelung und anschlieβend der Phosphatierung, jeweils in Kombination mit Spül- und Regenerator-Systemen, wurde jeweils eine Superstruktur, die alle sinnvollen Gestaltungsalternativen und die Vernetzungen innerhalb des Systems darstellt, entwickelt. Im Bezug auf diese Superstrukturen werden die Sachbilanzen erstellt und dazugehörige Kosten- und Energiegleichungen ermittelt mit Rücksicht auf Prozessanforderungen. Mittels dieser Gleichungen wird ein Systemmodell in gemischt ganzzahlig nichtlineare Programmierung (MINLP) in GAMS modelliert.

Ergebnis ist in beiden Fällen ein Lösungsstrukturvorschlag, der im Vergleich zu den Referenz-Standardstrukturen um 20-25% kostengünstiger und gleichzeitig im Bezug auf die sensibelsten Umweltindikatoren ca. 50% umweltfreundlicher ist.

Die vorgelegte Arbeit bietet ein Hilfsmittel/Instrument zur Entscheidungsverfahren und strategischen Plannung durch systematische Analyse von Prozessflussdiagrammen, welches die gleichzeitige Bewertung von Umweltrelevanz und Gesamtkostenstruktur des Systems in einer Prozessoptimierungssequenz erlaub und als eigenständiges Werkzeug in Expertensysteme eingesetzt werden kann.

# SUMMARY

Targeting sustainable production processes is a question of achieving more cost effective and environmental friendly material balances than being only an economic and environment orientated aim. For optimization approach this means solution of multi-objective problems. Therefore, the aim of this work is developing a general applicable optimization method, which enables the design of economic and ecological better processes and provides an instrument for e*co-process design*.

For integrated pollution prevention in metal finishing, pre-treatment line of automobile production is especially interesting, since it is wastewater and chemicals intensive. The process liquors, so called electrolytes contain usually metal salt ions like chromium, copper, nickel and zinc compounds and additives. Subsequently, the electrolyte rests that are dragged out with the work pieces will be rinsed off into rinse baths of the rinsing system.

In these rinsing systems considerable amounts of wastewater arise/ are produced which also means great amounts of water consumption/to be consumed. The content of rinse water is the drag-outs from process baths that cause depletion of raw materials/sources and as toxic chemicals (heavy metals) will tempt to pollute the environment.

For more sustainable design of metal finishing lines the required product quality should also be based on environmental consciousness and cost effectiveness of process alternatives. The pre-treatment stages include many sub-processes in sequence (n) that can be connected in various options (maximal $2^{n-1}$) that the variety of interconnections can not be compared to

each other. If n were 10, then this means up to 1023 different process possibilities to be considered.

With this motivation development of an ECO-optimization method, which is based on a superstructure that can consider both ecological and economic aspects simultaneously during process synthesis, comes out to be the central question of this work.

Its main result is an algorithm (*Simultaneous Analysis of Environmental Impacts Sensitivity*, SAEIS), that enables the ecological aspects to be quantified and then with total annual cost (TAC) of different process network configurations in a multi-objective function to be integrated.

First of all, quantitative scores as indicator results (Ti) for different environmental aspects are calculated. Then, a relative increase score (Ti'), representing a quantitative representation of environmental impact potential of the system, is obtained. Since the aggregation of environmental indicator results of substances regarding the ISO-14000 Standards is not allowed, a maximum relative increase score realized is used for a quantitative representation of environmental impact potential of the system. This absolute number represents the ecological criterion integrated into the multi-objective function of the SAEIS-Algorithm.

The implementation of this algorithm for optimized design of rinsing systems is demonstrated with two case studies of metal finishing line from automobile production. In process synthesis the superstructure of nickel plating and phosphating lines with their rinsing and recycling network is illustrated. This shows all potential configurations and interconnections within the system to which materials balances can be referred. In terms of these superstructure based balances cost and energy equations can be formulized considering the process requirements. Then, a system model in mixed-integer nonlinear programming is formed in GAMS by these equations.

The results of both cases represent different structural solutions, which are 20-25 % cost effective and at the same time 50% more environment friendly (with respect to the most sensible indicator) in comparison to the reference-standard case.

This presented work provides a tool for decision making and strategically planning in systematic analysis of process flow diagrams assessing a system's environmental relevance as well as eco-eco trade off. As a tool it can also be integrated into so called expert systems.

# CHAPTER 1 – INTRODUCTION AND AIMS

In the past it had been recognized that the environment and the socio-economic order are completely dependent on each other. To lower costs of production and to increase environmental friendlyness a variety of waste reduction techniques are applied (Lens et al., 2002). However, in recent years, economical incentives and the corresponding emphasis on prevention as a management priority have grown up rapidly because of image and marketing of the company. It was cheaper to dispose wastes into the environment without assessing the social costs of the pollution at the source. Industrialists pursue waste reduction as long as it was profitable.

Continued use of the environment led to pollution awareness in the 1960s and end-of-pipe controls (Salveski & Bagajewicz, 2000a). Investment costs for such technologies were partially offset. ‘Pollution controls solve no problem. They only alter the problem, shifting it from one to another, contrary to this immutable law of nature.’ (Koeningsberger, 1986). It is apparent that conventional controls, at some point, create more pollution than they remove and consume resources out of proportion to the benefits derived. It takes resources to remove pollution; pollution removal generates residue; it makes more resources to dispose of this residue and disposal of residue also produces pollution: a paradox (Shen, 1999).

Pollution prevention priorities are source reduction in a hierarchy of options addressing pollutants and wastes. Sustainable development has been universally accepted as our common environmental goal. To implement sustainable development, it requires promotion and application of pollution prevention through source reduction and clean technologies or furthermore process integrated optimization methodologies (Lens et al., 2002).

For producers in the economic system, ‘waste is a nonproductive stream of material or energy for which the cost of recovery, collection etc. to another use is greater than the value as an input’ (Shen, 1999). Pollution prevention should not be defined narrowly as source reduction or toxics use reduction. It should be considered more conceptually as any process that involves continous improvement and movement up the environmental management hierarchy.

At the end of 80s sustainable development was defined as ‘economic, social and environmental development that meets the needs of the present without compromising the ability of future generations to meet their own needs’ (Shen, 1999). Therefore, adequate availability of energy and resources is a prerequisite to achieve the socio-economic development. Important parameters for an intelligent use of material and energy sources are affordable costs, social acceptance and new industrial activities. The provision and use of resources, water and energy should in itself be consistent with pursuit of sustainability.

Dematerialization of the economy and the closing of resource and material cycles (so called zero-discharge) are popular policy concepts developed with the goal of managing resource and material flows.

*Zero Discharge:*

The feasibility of zero-discharge option in different industries is analysed in Koppol et al. (2003) for both single and multiple contaminant/component systems with available treatment technologies. It is concluded that zero-discharge can be feasible when regeneration has a small outlet concentration. Otherwise, recycles can exist with some discharge. Between the cases of a paper mill, an ethyl chloride plant, a petroleum refinery and a tricresyl phosphate plant only in the case of paper mill zero discharge was found to be possible and moreover profitable. In petroleum refinery and tricresyl phosphate plant cases large reductions in liquid discharge and operating costs could be met by reuse and regeneration of wastewater and in the case of ethyl chloride plant reduction in significant liquid discharge is achieved by a low-cost treatment technology. In conclusion, all cost of regeneration, cost of freshwater and the discharge concentration of the treatment are determining factors in structure and economical feasiblity of zero-discharge or partial liquid discharge cycles.

Zero discharge/emission combined with a retrofitting method for an existing galvanizing plant is recently discussed in Frenser et al. (2007) with more emphasize on rinsing conditions and spent solutions' recycling. From five considered plants in three of them the discharge of spent process baths could be fully avoided and in one plant zero emission has been achieved. In the other plant it was not economically feasible.

Thus, the scientific and technological challenges in the field of closing resource and water cycles are manifold. In general closing these cycles involve modifications of the production process. For example, adopting of green chemistry or clean technologies are the latest trials for sustainable production. Clean technology goes one step further than green chemistry and reevaluates the complete production process. It considers the life cycle of a product/material and attempts to minimise the use of resources as well as the amount of emissions during the life span of it. A conventional (clean-up) technology, besides reducing the environmental impact, increases the economical costs (Lens et al., 2002).

Nevertheless, by selecting clean technologies the current processes might be retrofitted completely. Thus, the environmental impact can be reduced at lower economical costs. Because of both aspects conflicting each other, sustainability leads to a multi-objective task.

Early environmental solutions to processes lacked cost effectiveness and sustainability. Further improvement in environmental operation of sustainable production led to analysis of plant mass balances, improved housekeeping around existing processes, and finally process redesign. This has also speculated to zero-discharge designs. It became clear that the costs and energy consumption increase as we get closer to 100 % removal of the pollutants (Stephenson & Blackburn, 1997). Due to the emphasis on cost considerations in best avaliable and applicable technologies by process design, zero-discharge can not often be a realistic solution. Cost and hidden wastes such as increased energy consumption are decisive for sustainable designs.

A further prediction for sustainable waste minimisation is that it must be based on insightful pollution prevention. This can be realised only by a thorough understanding of the technical, economic and ecological aspects of the process which adresses the root cause of environmental problems. The recent works in this field provide a systematic approach for the quantification of environmental impacts of the process by introducing life cycle assessment to multi-objective process optimization as one of the objectives (Khan et al., 2001).

## Aims

Sustainable development challenges the process design contrary to traditional design, which only meets the functional requirements. Therefore sustainability criteria for the significant processes should be identified, while the necessary material and process data should be provided. In many industrial branches it is awkward, especially if it meets their know-how. Modifications in process design can cause a loss in quality which is a sensible issue.

In this thesis a new integrated process design approach is introduced and demonstrated for metal finishing line case studies in automotive industry. Aim of this work is to generate a general applicable design/optimization method considering both ecological and economic aspects by Erol & Thöming, 2005; 2006.

The field of metal finishig was chosen for the case study because the line is chemical- and wastewater intensive. Generally process solutions in metal finishing are electrolytes that contain chromium, copper, nickel and zinc ions and various additives. Subsequent to pre-treatment stages in metal finishing line the drag-out that clings to the work pieces should be washed out by rinsing (Schmidt et al., 2000). Rinsing systems produce great amounts of wastewater, typically 0,352-1,34 L drag-out/m² product surface in a Watt's nickel plating rinse (Higgins, 1995), which also means same amounts of water consumption. Content of rinsing baths are actually the dragged-out bath-chemicals, thus these get lost in terms of ressources which also means contamination or pollution, esp. heavy metals.

Driving process design in metal finishing towards sustainability requires consideration of both environmental compatibility and cost-effectiveness besides quality furtherance. Since a metal-finishing line consists of a sequence of n process components that could be installed in many different combinations, each combination represents another dimensioning which could not be so easily compared. On this account it was the motivation for developing an ECO-optimization method that considers both ecological and economic aspects simultaneously in process synthesis based on the so-called superstructure of the system. The environmental impacts are to be quantified in figures in form of different environmental impact indicators. The most sensitive environmental impact category is derived to represent the environmental relevance of the system, since the aggregation is not allowed under the terms of ISO-14000 Standards. This representative maximum could then be traded-off with the total costs in multi-objective optimization by means of SAEIS-algorithm in order to realize a simultaneous ECO-optimization of rinsing systems in metal finishing line.

# CHAPTER 2 - BASICS

Since chemical engineering for unit operations reached a relatively mature state and sufficient experience is accumulated, formation of design heuristics and design analogy are enabled. Thus, computational power encouraged systematic methods and tools for process synthesis began to be developed (Barnicki & Siirola, 2004). Application for material substitution began to be saturated. But process synthesis tools, especially process integration tools were brought to bear. The process synthesis methods and tools that are developed in last decades, reached a level of maturity for providing advantage of practicing in an environment of increased costs and shrinking margins.

Future growth within production systems is likely to improve with aspects such as raw material and energy availability, climate change, mitigation, sustainability and inherent security. This manifoldness leads to multi-task design.

Decomposition of industrial process designs into a hierchical series of all subproblems such as reaction subsystems, basic material input-output-recycle structure, seperation and purification subsystems, environmental protection subsystems, and the like are the basics of current systematic generation approaches (Barnicki & Siirola, 2004) is intended because of the complexity of these design tasks. Since these interact in often complex ways, they can not be considered as entirely independent. The performance of future generation process synthesis methods and especially the optimality of the process design depends on the multitask concepts. Therefore process optimization leads to multi-objective optimization.

An optimization problem only in the context of environmental aspects is a single objective optimization like the conventional ones. However, if the source of environmental issues is considered, then a single objective (esp. wastewater) mostly turns out to be a multiple component system. A multiple component/contaminant network design is carried out with first designing sub-networks for significant component/contaminant. Targeting for each component/contaminant tells about what happens to this component/contaminant, but ignores the others' fate. In fact each sub-network incorporates some degradation in the concentrations of the other contaminants which can result in the next units' flowrates. However, it has been concluded that maintaining the features of each sub-network due to the wastewater degradation occurring in each sub-network is not always possible (Kuo et. al, 1997). Thus a multiple component/contaminant system is mostly preferred. Application for a retrofitting case requires a slightly modified objective including other options than the existing ones (Bagajewicz et al., 2000).

A multiple component/contaminant system considering all interaction within the system hands us in more explicit system analysis and synthesis, which is requisite for a superstructure optimization where removing of the unnecessary features is intended. Referring key components than a single component can provide some simplifications for the algorithmic procedure as it is done in Bagajewicz et al. (2000) and Salveski & Bagajewicz (2003). For some industrial optimization cases (Salveski & Bagajewicz, 2001) and particullary for water management issues with low concentrations as given in Salveski & Bagajewicz (2000b) it is also convenient to simplify the system and apply a single component system optimization with a measure of representative major quality parameter for wastewater flow since the treatment units are based on the type and concentration of its contaminants. In this case, the representative parameter covers the dominating pollutants of the system (Bagajewicz, 2000).

## 2.1. Basics of Mathematical Process Optmization

### *2.1.1. Multi-Objective Optimization*

Optimization means finding one or more feasible solutions that correspond to extreme values of one or more objectives. Finding such optimal solutions in a problem is valuable for engineering design, for scientific experiments, and business decision making (Ehrgott, 2005).

When an optimization problem involves only one objective function, the task of finding the optimal solution is called single-objective optimization. Today, existing single-objective optimization algorithms either employ gradient-based deterministic search principles or heuristic-based search techniques. The former approaches converge to local minimums. The latter on the other hand allow optimization algorithms to find globally optimal solutions.

When an optimization problem involves more than one objective function, the task of finding one or more optimum solutions is known as multi-objective optimization. Since multi-objective optimization involves multiple objectives, single-objective optimization can be thought as a special case of multi-objective optimization. Most real-world search and optimization problems involve multiple objectives. Then, different solutions present trade-offs (conflicting scenarios) among different objectives.

There exist many algorithms for system optimization and their application involving multiple objectives. However, the majority of these methods avoid the complexities involved in a multi-objective optimization problem by transforming multiple objectives into a single objective function by using user-defined weighing parameters. Thus, most studies in classical multi-objective optimization do not treat multi-objective optimization differently than single-objective optimization. In fact, multi-objective optimization is considered as an application of single-objective optimization for handling multiple objectives. There might exist a number of solutions that are all optimal. Without any further information, no solution from such a set of optimal solutions can be said to be better than the other. Since a number of solutions are optimal, in a multi-objective optimization problem many optimal solutions have to be considered. This is the fundamental difference between a single-objective and a multi-objective optimization task. The important solution in a single-objective optimization is the only optimum solution, whereas in multi-objective optimization, a number of optimal solutions might be found trading-off the conflicting objectives (Karslı, 2004).

In a multi-objective optimization, the purpose is to find the set of optimal solutions by considering all objectives to be important. After a set of such trade-off solutions are found, a strategic decision can be made. In the first stage, the task is to find as many different trade-off solutions as possible. Once a well-distributed set of trade-off solutions is found, second stage then requires certain problem information in order to choose one solution. Actually, second stage requires various subjective and problem-dependent considerations. There is also a progress in mathematical programming methods and software for solving optimization problems as in the development of powerful modeling languages (General Algebraic Modeling System, GAMS).

### Pareto Optimality - Domination

The swiss economist Pareto introduced Pareto optimality, at the turn of the previous century (Karslı, 2004). To illustrate the meaning of Pareto optimality, the concept of domination should be cleared. Most multi-objective optimization algorithms use the concept of domination. In such algorithms, all solution pairs compared with each other on the basis of whether one dominates other or not.

It should be mentioned here that there exist multiple Pareto-optimal solutions in a problem only if the objectives are conflicting to each other. In other words, if the objectives are not conflicting to each other, the number of the members of the Pareto-optimal set will be one. As seen in Figure 1, the curve formed by joining the Pareto-optimal solutions is called as Pareto-optimal front (Ehrgott, 2005).

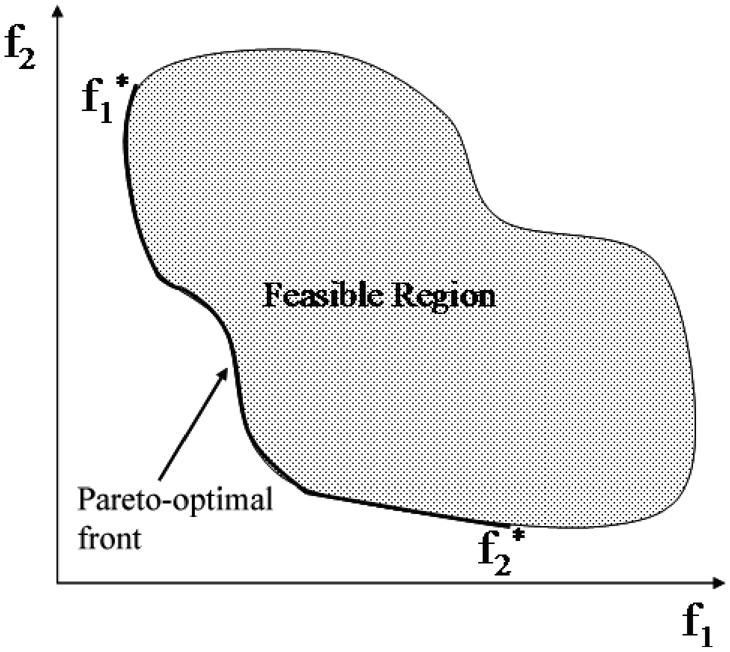

Figure 1: A Pareto-optimal front illustration
f1, f2: different objectives   f*: minimum of f1 & f2

Definition of optimization problem is so versatile that it can embed various aspects such as minimisation of system costs or maximisation of environmental performance of a system. In return the equality constraints include material and energy balances, process modelling equations or thermodynamic requirements. On the other side, the nature of inequality constraints may be environmental (e.g. concentration limits of certain pollutants), technical (e.g. pressure, temperature, or flow rate like technology specifications) and thermodynamic (e.g. driving force for mass, heat, or momentum transfer should be positive) (Rossiter & Kumana, 1995).

In a linear program (LP) the objective function as well as all the constraints are linear otherwise, it is referred to as a non-linear program (NLP). Regarding the nature of optimization variables the optimization program can be more classified. An optimization problem containing continous (real) variables (e.g. pressure, temperature, flow rate) as well as integer variables (such as 0, 1, 2…) is to be called mixed-integer program (MIP). Related to the linearity characteristics of the problem it can be further classified into mixed-integer linear program (MILP) and mixed-integer non-linear program (MINLP)[1]. The integer variables can be given in form of binary variables and helps to model logic events and decisions.

### ***2.1.2. Process Synthesis: Superstructure Optimization***

The process synthesis is basically represented by two approaches; hierarchical decomposition and mathematical programming (Grossmann, 1996; Grossmann et al., 2000). Each approach is concerned with different aspects of system design. The hierarchical decomposition technique divides the synthesis procedure into discrete decision levels in the order of superiority, with each subsequent decision level objective of minimizing ranked higher than the previous one. The economic potential of the project is then evaluated and a decision is made for the further synthesis. This method develops an initial base-case design applying heuristics, short-cut design procedures and the system's physical insight. An example in the field of waste minimization was already reported by Dantus & High (1996); Dantus & High (1999).

Mathematical programming approach applies optimization techniques for the selection of a configuration and design parameters for the system. This synthesis procedure, considering the sizes and operating conditions of units, supports not only the determination of the units which should be integrated into the system, but also the way how their interconnections should be ascertained. With reference to the above mentioned approaches, the former implies a discrete decision making with discrete and even binary variables, while the latter implies making a choice within a continuous space. Therefore, the synthesis problem refers to a nonlinear

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[1] The objectives of this program identify two types of variables; one is an integer variable corresponding to the existence or absence of certain units in the solution by help of binaries. The second is a continuous variable determining the optimal values of non-discrete design and operating parameters like flow rates, pressures, unit sizes etc.

discrete/continuous optimization problem and can be mathematically formulated as a mixed-integer nonlinear problem MINLP.

Process synthesis involves the generation of alternatives in all process engineering steps within the innovation process (Harmsen, 2004). For a unique process, this means the selection, arrangement, and operation of processing units so as to create an optimal scheme. In other words, it is an act of determining the optimal interconnection of processing units as well as the optimal type and design of units within a process system. The interconnection of processing units is called the structure of the process system. When the performance of the system is specified, the structure of the system and the performance of the processing units are not determined uniquely. Since the process synthesis task is combinatorial and open-ended, it has lead to development of quite different approaches such as thermodynamic targets (Linnhoff & Turner, 1981), heuristic (Douglas, 1985), evolutionary methods (Stephanopoulos & Westerberg, 1976), and optimization techniques (Grossmann & Biegler, 2004; Biegler & Grossmann, 2004). Therefore, this work will be dealing with the structural flow sheet optimization problem as it is defined in Biegler et al. (1997). Mathematical programming technique become interesting since it provides a systematic framework for process synthesis.

In 1980s, most of the process synthesis and design problems have been formulated as mixed-integer linear programming (MILP) problems. Because of the limitation that nonlinearities cannot be treated explicitly and approximated through the discretization there is a motivation for using mixed-integer non linear programming (MINLP). Thus a large number of process synthesis, design and control problems in chemical engineering can be modelled as mixed-integer nonlinear programming problems (Grossmann & Sargent, 1979; Kocis & Grossmann, 1987; Kocis & Grossmann, 1988; Kocis & Grossmann, 1989a; Kocis & Grossmann, 1989b; Floudas et al., 1989; Salcedo, 1992; Angira & Babu, 2006.)

However, due to the many varied interactions between the subsystems, the only way to explore these interactions integrally is to perform simultaneous synthesis of the overall process schemes using mathematical programming approach. The most efficient way to perform discrete and continous decisions simultaneously is to apply mixed-integer nonlinear programming (MINLP) (Bedenik et al., 2004). Although the optimality and feasibility of the solution, the direct synthesis of overall process scheme by MINLP is still limited by small size problems because of its complexity.

For the generation of flowsheet superstructure for a new design in process synthesis there are different methods, which can also be broadly either classified as algorithmic and/or heuristic systematic generation methods (Kovacs et al., 2000). Both categories could be followed by an evolutionary modification step as it is defined in Siirola, 1996. Some systematic generation approaches, which decompose the design into a hierarchical series of subproblems in terms of artificial intelligence (AI) paradigm in design generation for providing design alternatives, are introduced in Barnicki & Siirola, 2004. Here AI paradigm enables the incorporation of new representations of underlying physical sciences, new social concerns and new design strategies into process synthesis algorithms. Another approach is the superstructure optimization for analyzing the alternatives to find the "best" solution between other potential alternatives by trading-off both economic and ecological aspects in decision making phase (Erol & Thöming, 2005; 2006).

### *2.1.3. Process Integration*

Future industrial process design enterprise is likely to involve many steps and interact with many aspects towards sustainability. Generally issues of process controllability, operability and flexibility are considered after the first invention and analyzing of the resulting design. Process integration of such aspects and sustainability may be integrated into the process synthesis procedures themselves rather than be considered after synthesis and optimization of the process.

The sequence of the integrated process design is discussed in general and new ideas for alternative approaches are introduced in Lewin et al., 2002. The systematic of process integration is characterized in cognitive levels such as knowledge, comprehension, application, analysis, synthesis and evaluation. The need to integrate process control with process design is stressed in Edgar et al. (2001) and Rhinehart et al. (1995). In Lewin et al. (2002) it is also underlined to have a balance between heuristics and computer-aided algorithmic methods for acquired experience of designing practical processes with critical generation of optimal designs.

Various applications of process integration with expert systems for the last decade are broadly reviewed in Liao (2005). Some applications have overlapping of different methodologies such as training, knowledge acquisition, knowledge representation, knowledge learning, production planning, system design/development, modelling, process control, decision making, waste treatment, resource management, forecasting, ecological planning, chemical application, industry planning, management issues, and knowledge reuse. Integration of qualitative, quantitative and scientific methods throughout process integration broadens the horizon on process design and obtains new understanding methodologies. A case specific process integrated tool for metal processing is introduced in Szafnicki (2005).

### *2.1.4. Eco-optimal Process Integration*

Minimizing environmental impacts is supposed to be achieved by reusing or recovery of the resources as much as possible. When high quotes of recycling are aimed, this task is linked to hidden wastes such as energy consumption and high costs (Cohen & Overcash, 1995). In the course of high energy consumption, there are both ecological burdens and economical charges. This dilemma of conflicting aspects indicates that a multi-objective optimization, allowing an "eco-eco" (ecological and economic) trade-off can be an option.

This debate on multi-objective optimization is investigated by means of two basic approaches; the first one, namely the performance of an impact assessment, such as the standard life cycle assessment procedure followed by an evaluation of the most environmental benign system between the alternatives (Shonnard & Hiew, 2000) and the second one, in which more process integration methodology in the form of final comparative assessment is applied (Bagajewicz, 2000; Alva-Argaez et al., 1998; Dantus & High ,1999).

Another multi-objective optimization methodology adresses the same problem type performing series of single objective optimization on condition that all objectives except one are converted into constraints (Azapagic, 1999). A hybrid methodology application for minimization of cost and emissions, where a minimization of single objective optimization problems algorithm is developed, has been introduced through the work of Diwekar & Fu, 2004. Further development, in which a combination of single objective and multi-objective optimization debated within a two layer algorithm for performing a hybrid method, is discussed in Kheawhom & Hirao, 2004. It should be noted that, this combination of single and multi-objective optimization is supported by a computer-simulation model that handles the uncertainty using multi-period and stochastic optimization formulations.

The inherent disadvantage of hybrid methodologies is the requirement of quantitative weighting factors that are prone to individual interpretations and the subjectivity by ranking that is involved. However, in most instances both economic and environmental objectives are aggregated into a single objective function using the analytical hierarchy process (AHP) (Chen et al., 2002). A hybrid approach consists of both quantitative and qualitative weighting.

All these methodologies provide relationships between mathematical programming and decision support systems leading to an expert system (see in Figure 2). An example of such an environmental decision support system is developed by Rizzoli & Young (1997), which integrates both the identification of the general attributes of the environment and the system and simulation models. Similarly, to aid the decision making in the area of facility planning management, Han et al. (1991) developed a combination of mathematical optimization model with a database management system as an expert system. In this work an ECO-optimization approach is introduced that can lead to a decision support tool in modelling category of the expert systems, as it is categorized in Liao (2005).

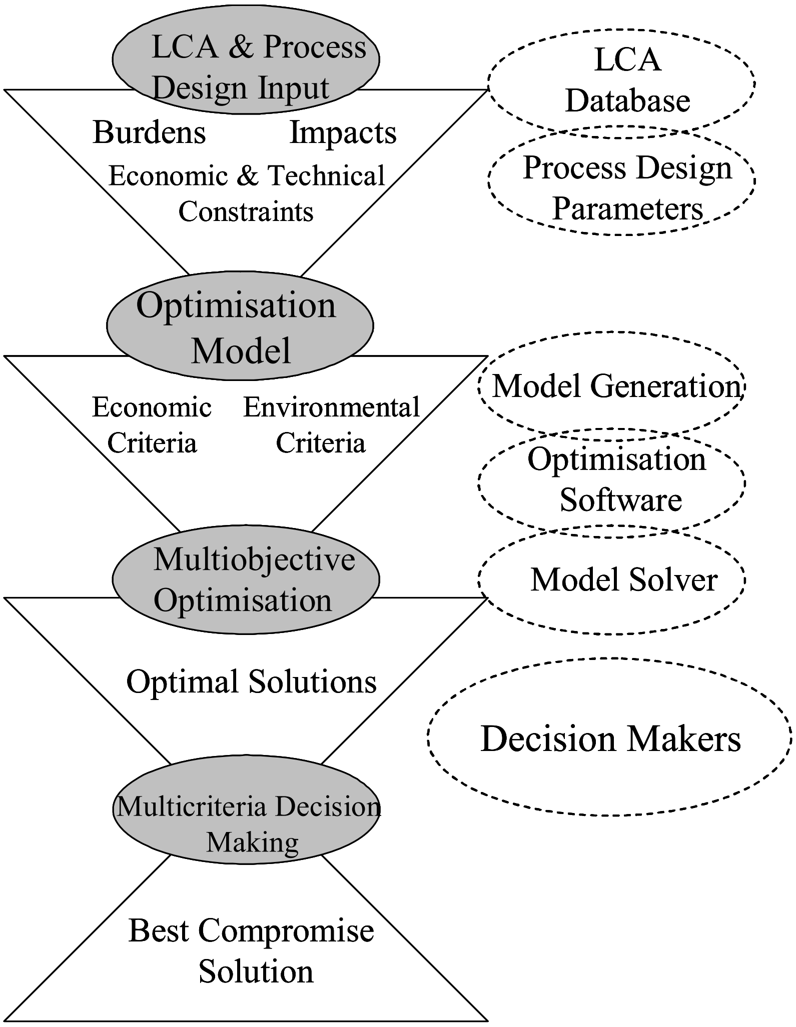

Figure 2: General methodological framework for integration of LCA in process design

In this work a new approach is suggested, a hybrid form of both methodologies that integrates impact assessments, such as environmental considerations and socioeconomic factors with process synthesis by means of multi-objective optimization.

New process synthesis paradigms incorporating more effective representations of the underlying physical sciences and engineering art, new social concerns, new design strategies, and new computerized implementations may be developed by advances in artificial intelligence.

A collaboration of the systematic generation and superstructure optimization process synthesis paradigms may be done in which systematic generation is used to create the superstructure for simultaneous dicrete and continous variable optimization.

Resulting process designs could certainly be evaluated from additional points of view including social considerations, so that superstructure optimization will need to produce families of good designs for multi-criteria Pareto optimization. There are many challenges, but continued progress will be made and these challenges will be met.

For the evaluation of process designs there is a number of different viewpoints including, of course, economics, but also health and safety, environmental impact, energy consumption, controllability, flexibility, ease of construction and maintainability. It is very likely that even more social factors may become important in the future, including sustainability, life cycle impact, climatic impact and risk minimization.

In some cases competing factors can be reduced to a common denominator, for example costs and benefits, with trade-offs incorporated into an economic optimization objective function. More often the various factors cannot be rationalized and may not be uniquely quantifiable. Probably design selection will involve multi-criteria optimization and evaluation of Pareto sets. This will pursue the synthesis system to generate rather whole families of designs, particulary involving different chemistries than only an economic optimum design. Each may need to be evaluated from distinct point of view, or with yet-to-be-developed optimization objectives that somehow incorporate social criteria.

## 2.2. LCA as a Tool in ECO-Optimization

Life Cycle Assessment as it is defined in the ISO (International Standards Organization) - 14040 (DIN EN ISO 14040, 1997), is a technique for assessing the environmental aspects and potential impacts associated with a product, by compiling an inventory of relevant inputs and outputs, evaluating the potential environmental impacts associated with those inputs and outputs and interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study.

As it is stated in ISO 14040, LCA can also assist in identifying opportunities to improve the environmental aspects of products at various points in their life cycle and decision-making in industry for strategic planning, priority setting, product or process design or redesign and for selection of relevant indicators of environmental performance. Besides being applied to products and their life cycle, it can be used for assessing the environmental aspects and potential impacts associated with process flow, process method or plants.

Additional details regarding methods are provided in the complementary International Standards ISO 14041, ISO 14042 and ISO 14043 concerning the various phases of LCA such as goal and scope definition and life cycle inventory analysis, life cycle impact assessment and life cycle interpretation.

For systematic assessment of environmental aspects, methods that provide environmental objectives to be incorporated into hybrid methodology used in expert systems include Life-

Cycle Assessment (LCA) (SETAC, 1993), waste reduction algorithm (Mallick, 1996), methodology for environmental impact minimization (Pistikopoulos et al., 1995) and environmental fate and risk assessment tool (Shonnard & Hiew, 2000).

The environmental impact assessment methods like Eco-indicator 99 (as shown in Figure 3), Eco-points, problem-oriented approach (LCA, 2001), which are used to calculate the indicators (Ti) for each environmental impact category, differ according to their main focus in defining the category indicators. Eco-indicator 99 and other impact assessment methods provide such an approach with partly different impact categories and category indicators. Problem oriented approach is driven by environmental problem (so-called mid-point of the cause-effect chain) rather than by damage (the end point of this chain).

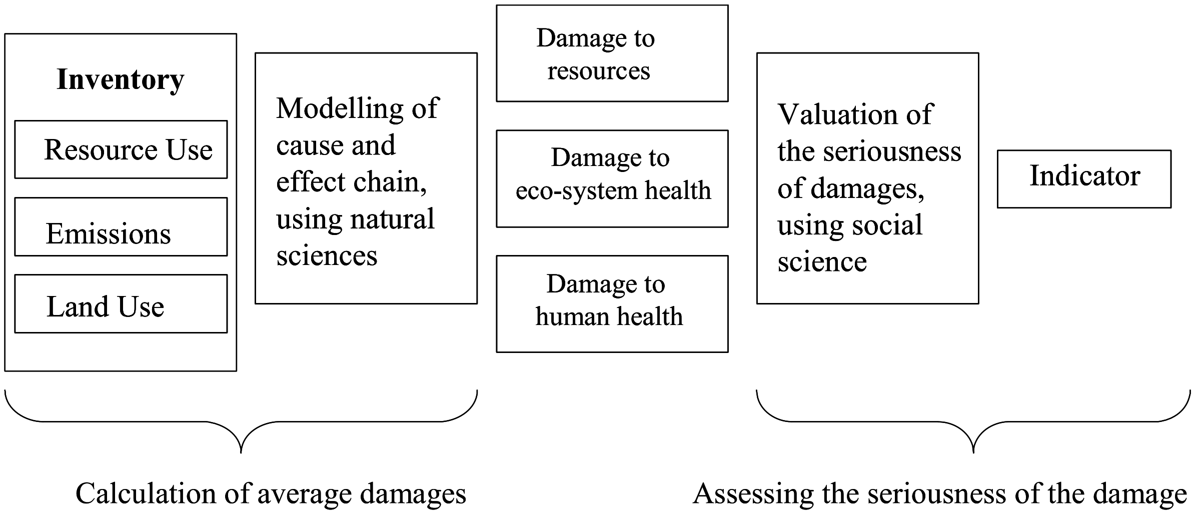

Figure 3**:** The core concept of the Eco-Indicator methodology (Goedkoop et al., 1998; Goedkoop & Spriensma, 1999)

The four stages: goal definition and scope; inventory analysis; impact assessment and improvement assessment as shown in Figure 4 depicts a framework for conducting LCA that was developed by the Society of Environmental Toxicology and Chemistry (SETAC, 1993). It is an integrated approach that aims to avoid to substituting one set of environmental problems for another set. They define LCA as ‘a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; assessing the impact of these energy and material uses and releases to the environment; and identifying and evaluating opportunities to affect environmental improvements'. The International Organization for Standardization (ISO) started similar work on developing principles and guidelines for LCA (ISO, 1997).

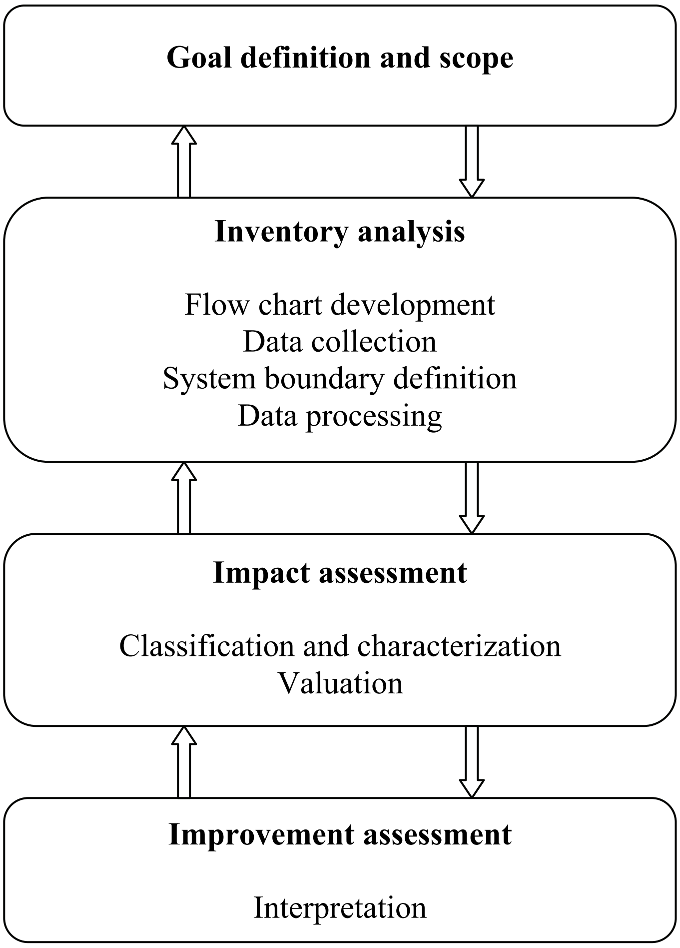

Figure 4: Life Cycle Framework according to ISO 14001

Although SETAC and ISO worked independently, a general consensus on the methodological framework between the two bodies has started to emerge. While the ISO methodology is still being shaped, the methodology developed by SETAC remains widely accepted among the LCA practitioners (Khan et al., 2004).

In ECO-Optimization concept some phases of LCA will serve as a tool for decision-making and strategic planning like in Burgess & Brennan (2001) throughout systematical analysis of process flow networks, which are defined by means of hyperstructures based on material balances. Life Cycle Inventory Analysis (LCIA) phase of LCA will be used to examine the product system from an environmental perspective using category indicators.

LCIA assigns LCI results to impact categories (classification). For each category the indicators are selected and the category indicator results, hereafter referred to as indicator results, are calculated. The collection of indicator results, hereafter referred to as the LCIA profile, provides information on the environmental relevance of the resource use and emissions associated with product system.

### *Problem-oriented Environmental Impact Assessment Method*

The environmental profile resulting from the characterization step will be calculated with different characterization models and factors. These environmental impact assessment methods differ according to their main focus on defining the category indicators.

In Ecopoints method emissions and extractions are weighted using a distance-to target method i.e. based on policy targets. A second method focuses on the point in the environmental mechanism at which the categories are defined. They may be defined close to the intervention and called the mid-point, or problem-oriented approach or at the level of category end points and called the end-point, or damage approach.

In the last decade many efforts have been done for developing these models and category indicators. The most comprehensive and recent work of these is the Eco-indicator 99 by Goedkoop & Spriensma (1999). In stead of working with many indicator results the Eco-indicator employs only 1 to 3 weighted indices. Thus there is more emphasis on weighting than the other approaches. Three types of damage are considered for which weighting is more readily feasible that are damage to resources, damage to ecosystem quality and damage to human health.

Although the Eco-indicator 99 approach is very promising and is certainly appealing as an avenue for further research, the problem-oriented approach is currently deemed the ‘best practice’ for impact assessment (LCA, 2001). Since the problem-oriented approach with impact categories defined at the midpoint level allows the best available indicator to be used for each impact category, this category indicator is defined regardless of where in the environmental mechanism between intervention and endpoint.

## 2.3. Basics of Pre-Treatment in Metal Finishing

Metal surfaces in process plants are usually coated with oxides, grease or dirt arising from prior operations such as working, storage and transport. This causes a need to have a pre-treatment in order to achieve a sufficiently cleaned surface which suites consequent process requirements.

Metal-finishing operations involve many single steps such as cleaning, degreasing, pickling, electroplating and electroless metal plating, etching, passivation, phosphating and chemical electro polishing.

Each operation is typically followed by rinsing operation in which the parts are rinsed to remove finishing solutions that adhered to the parts (drag-out) and produces dilute waste stream. Rinse water is typically the predominant wastewater stream at plating facilities. The rinse water can be used for making up for evaporation losses in plating tanks, resulting in metal recovery and reduced waste discharge.

The metal-finishing processes themselves produce several waste streams containing acids and bases, toxic heavy metals, solvents and oils. Spent chemicals or metals and solvents are the principal components considered underneath wastewater treatment and hazardous waste regulations. Metal recovery and bath maintenance practices are usually done by using concentration processes such as evaporation, ion exchange, reverse osmosis, and electrodialysis. The main process and waste streams with its major material flows in metal finishing are illustrated in Figure 5. The workpiece flow directions through each process step also represent the drag-out carried over from one process bath to next one.

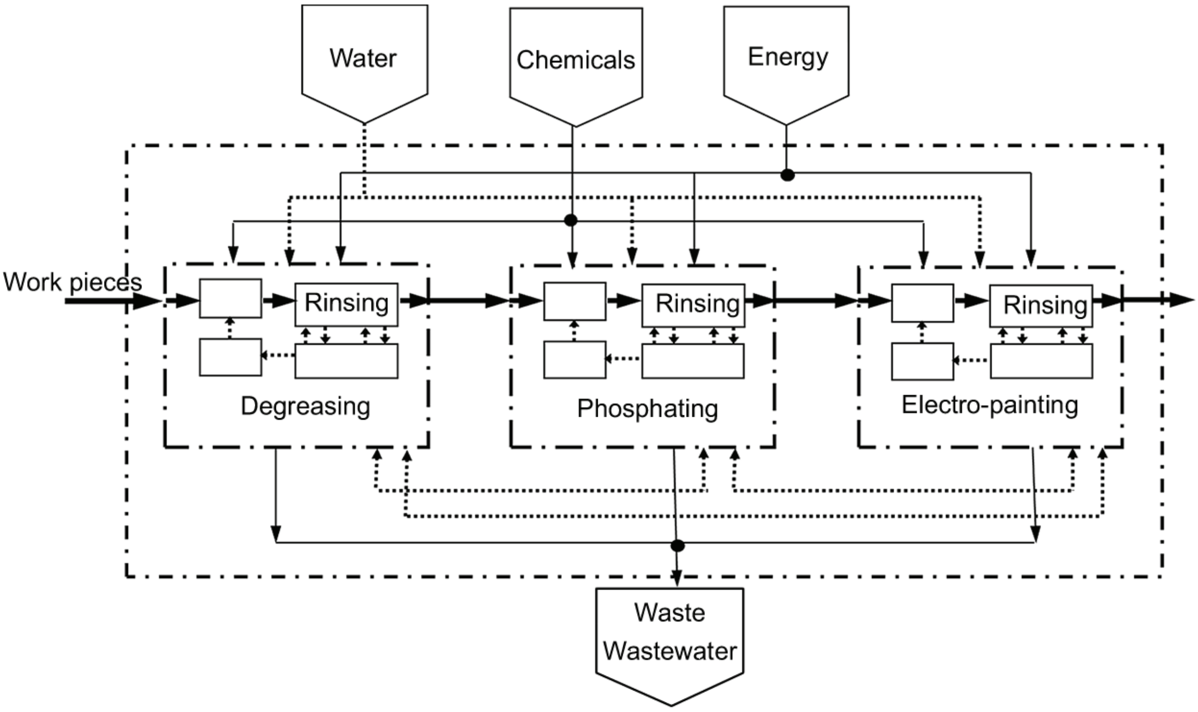

Figure 5: Entire superstructure of an integrated pre-treatment system prior to painting (Erol & Thöming, 2006)

Pre-treatment stages in metal finishing have significant energy, chemical and water consumption (Weng et al., 1998). This is especially true for different phosphating processes, which are among the most widely used pre-treatment processes of metal finishing in industrial practice (cf. Figure 5) for the purpose of improving the adhesion and service life of surface coatings under corrosive conditions on metal bodies prior to painting. For a uniform pickling effect, a prior degreasing and cleaning in aqueous alkaline or organic solutions is a necessity.

Towards more sustainable processes, conservation of resources within production lines is an important task. The main targets of applying recycling and reuse facilities are the saving of chemicals, freshwater and energy consumed. Since the applicability of such savings depends on their economical strength, there is need to integrate the environmental compatibility and the feasibility of systems simultaneously in the process design.

### *2.3.1. Nickel Plating*

Nickel plating is the most popular and useful metallic coating because of its combined physical and chemical properties (Higgins, 1995). Thin nickel coatings are mainly used for corrosion protection, for improving the ability to braze or solder difficult materials as an undercoating for other metal deposits that subsequently are plated. Heavy nickel coatings are used primarily for combined corrosion and wear resistance, salvage of worn or corroded parts, and electroforming. The mechanical properties of the nickel deposit and its effect on the base material (e.g., tensile strength, internal stres, ductility, and hardness) depends on the chemical composition and the operation of the plating bath. Watts nickel plating and duplex nickel plating are also used as undercoatings (Higgins, 1995; Freeman, 1995).

*Nickel Plating Solutions:*

There are different types of nickel plating solutions like sulphate, high chloride, all chloride, fluoborate and sulfamate solutions. This common nickel plating bath, is the sulphate bath as Watt's bath described below, with its typical composition and operating conditions. The large amount of nickel sulphate provides the necessary concentration of nickel ions. Nickel chloride improves anode corrosion and increases conductivity. Boric acid is used as a weak buffer to maintain the pH.

As it is seen in the following bath parameters (Anonymous 1, 2003) like nickel sulfate ($NiSO_4 \cdot 6H_2O$): 150-300 kg/m$^3$, nickel chloride ($NiCl_2 \cdot 6H_2O$): 45-90 kg/m$^3$, boric acid: 30-45 kg/m³, pH range: 2.0-5.2, temperature: 305 - 344 °K, current density: 0.9-5.57 A/m², Watt's nickel bath contains nickel compounds in salt (soluble) form that are classified as a reproductive toxicant and carcinogenic in a category 3 carcinogen in classification terms (Anonymous 2, 2003). Considering the hazard properties of nickel in process solution, nickel plating baths are typically followed by rinsing system combined with regeneration units for different purposes such as bath make up, bath solution recycling and rinse water recycling. As regenerator units ion-exchanger (IX), electro dialysis (ED) and reverse osmosis (RO) are used (Thöming, 2002; Higgins, 1995).

### *2.3.2. Phosphating*

The principle of phosphating depends on a treatment with an aqueous solution of an inorganic acid, the so called pickling. This method converts the oxides tightly adherent to the metal surface to a soluble form that can be removed by a rinsing process. Usually in practice, pickling with phosphoric acid works in two stages. At first, the work piece is deeped into a 15 to 20 % wt. concentration, in which both the formation of soluble iron-phosphate and removal of the impurities from the surface take place. This is then followed by passivation that occurs in a 1 to 2 % wt. solution and forms a protective secondary and tertiary phosphate film on the metal surface.

The initial basic chemical reaction involved in phosphating process describes acid attack on the metal surface (cf. Equation (2.1): Metal ionization).

$$2H^+ + M \rightarrow H_2 + M^{2+} \quad (2.1)$$

$$2(H_2PO_4)^- + 3M^{2+} \rightarrow M_3(PO_4)_2^{2+} + 4H^+ \quad (2.2)$$

In this reaction acid neutralization takes place (pH rises) with the increase in concentration of metal ions ($M^{2+}$) (Cape, 1987). During the subsequent reaction, the production of metal ions

$M^{2+}$ and the resulting consumption of acid cause a precipitation of divalent metal salts (cf. equation (2.2): Precipitation).

These reactions can be accelerated and improved by introducing a mechanical and electrolytic action, which can unfortunately concurrently result in a very active surface, on which fresh rust very readily forms. To limit this effect a combination of pickling and passivating action is desired. On account of its film-forming properties, phosphoric acid is often a preferred pickling agent.The passivation film formed during phosphating provides at least a temporary protection against corrosion and a surface suited to an organic coating.

To achieve better phosphating coating and corrosion resistance, certain accelerators and additives (e.g. refiner agents, surfactants) are incorporated into the bath solution resulting in varying bath compositions. The type of bath accelerator used differs according to the applied phosphating technique, such as immersion and spray processes. However the commonly used accelerators are nitrite, nitrate, chlorate and hydrogen peroxide, among these the most widely used accelerators are nitrite/nitrate and chlorate accelerators (Rausch, 1990; Freeman, 1995).

The relative importance of accelerators to the phosphating quality was pointed out by Sankara (1996a), who discussed the detrimental effect of concentration fluctuations. As a consequence of the intensive implementation of phosphating as a pre-treatment process, the potential environmental burden of process occurs by the chemicals and large amounts of consumed water and energy; thus there is a need for a systematic assessment method for these potential environmental impacts (Weng et al., 1998).

In recent developments in metal finishing techniques, the phosphating formulations are modified by incorporation of additives like nickel and/or manganese ions to suit the needs of the electrophoretic paint finishing (Sankara, 1996b). It has been observed that the inclusion of manganese and nickel ions in zinc phosphating bath causes the refinement of the crystal size and improvement of the corrosion resistance of the resultant phosphating coating. Other additives such as calcium modified zinc phosphating lead to the reduction in grain size and the improvement in compactness of the coating and corrosion resistance. Moreover such modification results in the development of trication phosphating bath as an alternative to the recent conventional phosphating processes in metal finishing (Sankara, 1996a).

Such a "trication phosphating", low zinc phosphating with additional manganese and nickel ions, with immersion processing is selected as a case study. In this phosphating solution, products such as Zn(II), Ni(II), Mn(II), phosphoric acid, oxidation agents like chlorate-($ClO_3^-$) and chloride- (Cl-) ions are to be found (Brouwer et al., 1999).

In its current form, the considered process consists of an immersion zinc phosphating bath followed by three rinsing stages and a precipitation unit for metal ions (Zn, Ni etc.). Rinsing stages generate wastewater containing additives and their degradation products at relevant concentrations [mg/l] like $Zn^{2+}$:115, $Ni^{2+}$:57, $Mn^{2+}$:59, $Na^+$:430, $H_2PO_4^-$:1500, $ClO_3^-$:200, $Cl^-$: 300 (Brouwer et al., 1999). Also for the precipitation stage there is considerable amount of chemical consumption.

For a more sustainable phosphating process, the common rinsing system could be substituted with zero-water discharge rinsing and recovery network (RRN) introduced by Thöming (2002). Since the zero-water discharge RRN are energy intensive, there is a demand to find a method to identify optimal process design with respect to wastewater production, energy demand and cost which leads to ECO-reuse and recovery networks (ECO-RRN) (Erol & Thöming, 2005).

*Practiced regeneration techniques:*

Various kinds of membrane processes can be applied for different purposes of environmental impact minimisation. For conditioning of rinse water mostly reverse osmosis technique is preferred. Rarely nanofiltration is used for recycling and reuse cases as alternative to ion exchangers, which usually enables recycling-loops in metal finishing. Due to the large amounts of wastewater produced during the regeneration, the cost effectiveness and environmental compatibility of these systems are to be discussed. Retreatment of process solutions for the purpose of refreshment is done by different membrane processes (separation). For instance, microfiltration respectively ultrafiltration are used for alkaline degreasing baths' refreshments (Schmidt et al., 2000).

Especially for the case of three cationic phosphating, reverse osmosis can be applied to remove the carryover substances from phosphating liquor and to produce a water quality of potable water referring to the patent DE 198 13 058 A1 (Brouwer et al., 1999). In another patent DE 197 43 933 A1 (Schultze & Marquaro, 1999) the application of nanofiltration for recovery of concentrate from the process liquor is suggested. Both these patents and Holmes (2002) illustrate the connection of nanofiltration (NF) and reverse osmosis (RO) in series. Therefore, for the phosphating case study (chapter 2.3.3) this coupling of nanofiltration (NF) and reverse osmosis (RO) is considered as regeneration system.

# CHAPTER 3 – METHOD DEVELOPMENT

In this work a structural presentation of material flow network called superstructure is made (El Halwagi, 1997). This technique embeds all potential configurations of interest and the interconnections within the system.

## 3.1. Process Synthesis

### *3.1.1 Superstructure*

In order to formulate the synthesis problem as a mathematical programming problem, a superstructure is postulated which includes many alternate designs from which the optimal process will be selected. Once the superstructure is specified, the next task is to determine the optimal process flow sheet through structural and parameter optimization of the superstructure, which requires the solution of a mixed integer optimization problem (Angira & Babu, 2006).

In this work rinsing recycling network (RRN) superstructure design problem was handled as follows: The necessary operation units for water usage and treatment, contaminants and freshwater sources are determined with heuristics from experience. Then, all possible network connections are introduced with mixing and splitting points. Prior to each operation a mixer and behind each operation a splitter are placed (see Figure 6).

Fresh water and drag-outs entering the network is split towards all operations and corresponding effluent streams generated from each operation are mixed and brought up to a final discharge point. After setting up all possible network allocations an optimization is to be carried out to reduce the system structure by removing irrelevant and uneconomical connections.

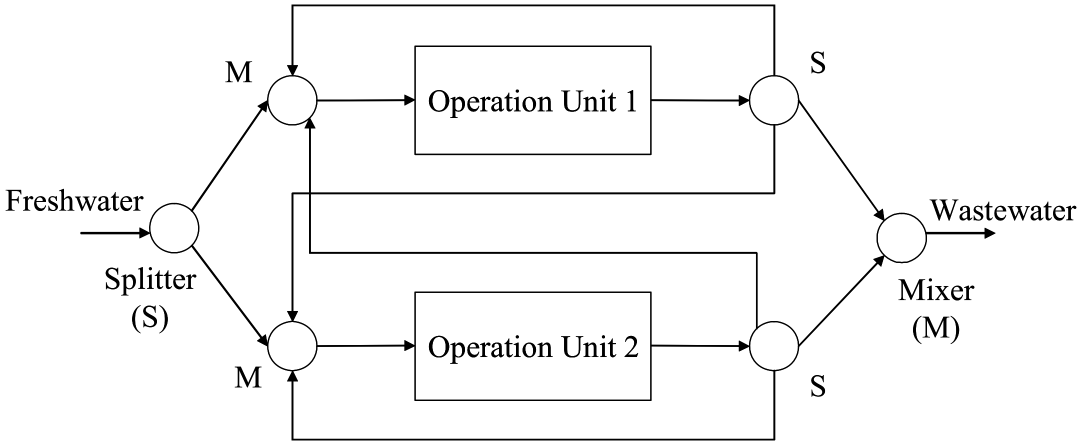

Figure 6: An illustrative core superstructure

### *3.1.2. Mixed-Integer Nonlinear Programming (MINLP) and Multi-Objective Optimization*

Process design and synthesis problems give rise to discrete/continuous optimization problems, which in algebraic form, correspond to mixed-integer optimization problems that have the following form:

$$\min f(x,y) = [f_1,f_2, \ldots,f_n] \tag{3.1}$$

$$\text{subjected to} \quad h(x,y) = 0$$

$$g(x,y) \leq 0 \qquad x \in R^n,\ y \in \{0,1\} \tag{3.2}$$

Here f is a vector of economic and environmental objective functions, where x and y are the vectors of continuous and integer (discrete) variables, respectively. h(x,y) = 0 represents the equality constraint such as energy and material balances. Besides g(x,y) ≤ 0 as the inequality constrain may describe material availabilities, capacities, etc. A vector of n continuous variables may include material and energy flows, pressures, compositions, sizes of units etc., while a vector q integer variables may be represented by alternative materials or processing routes in the system.

If the integer set is empty and the constraints and objective functions are linear, then Eqs. (3.1) and (3.2) represent a Linear Programming (LP) problem; if the set of integer variables is nonempty and nonlinear terms exist in the objective functions and constraints, Eqs. (3.1) and (3.2) is a Mixed-Integer Nonlinear Programming (MINLP) problem. If it incorporates only integer and linear variables, then the problem is a Mixed Integer Linear Programming (MILP) problem.

A system model in form of a mixed-integer nonlinear program (MINLP) is then developed by using material and compound balances with reference to the superstructure. According to the process requirements and heuristic rules the system boundaries are defined.

In the mathematical model for ECO-Design concept the environmental objective is provided by some phases of LCA which serves as a tool for decision-making and strategic planning (Burgess & Brennan, 2001) throughout systematical analysis of process flow networks. The economical objective is defined as a function of total annualized costs (TAC) considering each process unit in the network. The assessment of economical aspects is covered by TAC, including investment and operational costs of the plant.

A Pareto Optimal Solution Set has to be found within the given constrains that provides a base for decision making among the solutions. To find a Pareto optimal solution in this work a weighting method is applied, which allows the optimization of the model simultaneously (Sing, 1996). Making use of weighting factors α (alfa) and β (beta) that give the relation between both criteria, an objective function is built (Miettinen, 1999). The MINLP was written in GAMS version 21.2 and version 23.1 using the SBB solver to calculate the solution set.

## 3.2. Life Cycle Assessment (LCA)

Life Cycle Assessment (LCA) is defined as ‘the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle’ in ISO 14040 Standards. Thus, LCA is a tool for the analysis of the environmental burden of products at all stages in their life cycle (LCA, 2001).

LCA is, as far as possible quantitative in character; where this is not possible, qualitative aspects can – and should – be taken into account, so that as complete as possible a picture is given of the environmental impacts involved.

The core characteristic of LCA is its ‘holistic’ nature, which is both its major strength and, at the same time, its limitation. Analysing the complete life cycle of a product can only be achieved at the expense of simplifying other aspects. LCA for time aspect is typically steady-state, rather than a dynamic approach. Furthermore, LCA focuses on the environmental aspects of products, and do not support their economic, social and other characteristics. Since environmental impacts are not specified in time and space, they are often seen as ‘potential impacts’ and are usually related to an arbitrarily defined functional unit.

LCA involves a number of technical assumptions and value choices, despite its aim to be based on science. ISO standardisation process helps here to avoid arbitrariness and try to these assumptions and choices as transparent as possible. This is also for embedding LCA in procedures.

Nature of LCA as an analytical tool provides information for decision support. It can not replace the decision process itself. LCA in a decision making sequence is more adequate for a single substance. Nevertheless, combination of different tools in one decision making process is certainly valid (LCA, 2001). The main applications of LCA are: analysing the origins of problems related to a particular product/process; comparing improvement variants of a given product/process; designing new products/processes and choosing between a number of comparable products/processes. Similar applications can be distinguished at a strategic level. The way a life cycle assessment is implemented depends on the intended use of the LCA results. This can be a whole technical system analysis, not just the product; a whole material cycle along the product's value chain and not just a single operation or processing step for a product (e.g. refining of raw materials); a number of relevant environmental and health effects for the whole system and not just one individual environmental parameter (e.g. emissions of solvents, or particulates) (Kjaerheim, 2005). A further application in relation to products is the design of more environmentally friendly products, otherwise known as eco-design.

### *3.2.1. LCA as a Tool for Process Selection and Process Design*

Although the use of LCA has traditionally been oriented towards improving the environmental performance of products, several authors have recently demonstrated the previously unexplored potential of LCA as a tool for process selection and process design. A more detailed exposition of the application of LCA to process selection and design is given in [Khan et al., 2004]. Here, the focus is on the use of LCA for design process and optimization.

Life cycle assessment represents an approach normally used in selection and design processes. Although designing and optimization of a process by incorporating LCA represents slight incremental effort, recent literature suggests that LCA is gaining wider acceptance in many industrial sectors, particularly in the process industries. Some other examples of the use of LCA in corporate decision-making include energy; nuclear, water; electronic and other industries (Khan et al., 2001).

Applied to process design and analysis, LCA can have two main objectives. The first is to quantify and evaluate the environmental performance of a process from 'cradle to grave' and so help decision-makers to choose between alternative processes and processing routes. In this context, LCA provides a useful tool for identifying the Best Practicable Environmental Option (BPEO). Another objective of LCA is to help identify options for improving the environmental performance of a system. This objective can be of particular importance to process designers and engineers, because it can inform them how to modify a system to decrease its environmental impacts. To assist in identification of the optimal option for improved system operation from ‘’cradle to grave’’, LCA can be coupled with optimization techniques as discussed in the next section.

LCA considers the whole material and energy supply chains, so that the system of concern becomes everything within the system boundary. The material and energy flows that enter, exist in or leave the system include material and energy resources and emissions to air, water and land. These are often referred to as environmental burdens and they arise from activities encompassing extraction and refining of raw materials, transportation, processing, use and waste disposal of a product or process. The potential effects of the burdens on the environment, i.e., environmental impacts, normally include global warming potential (GWP), acidification, ozone depletion (OD), eutrophication, etc. The LCA methodology is still under development. At present, the methodological framework comprises of four phases (Azapagic & Clift, 1999a).

- goal and scope definition or, in other words, selection of the boundary – selecting the system boundaries to ensure that no relevant parts of the system are omitted;
- inventory analysis – performing mass and energy balances to quantify all material and energy inputs, wastes and emissions from the system, i.e., the environmental burdens;

- impact assessment – aggregating the environmental burdens quantified in the inventory analysis into a limited set of recognized environmental impact categories, such as global warming, acidification, ozone depletion, etc.; and
- interpretation of the results to reduce the environmental impacts associated with the product or process.

### *3.2.2. LCA and System Optimization*

Use of elaborate mathematical modelling is often necessary for describing and predicting the behaviour of complex industrial systems. The optimization technique essential can be rendered by identifying the optimum operating conditions that will ensure the improved process performance. In previous decades, system optimization in chemical and process engineering applications has only focused on maximising the economic performance subjected to certain constraints in the system. Over the last decade, more interest is shown on optimization of environmental performance alongside traditional economic performance and its incorporation into system optimization (Azapagic & Clift, 1999b).

Incorporating the economic and environmental performance led the optimization problem be multi-objective optimization problem. Thus the nature of LCA, there are also a number of distinct environmental burdens or impacts to be considered. A multi-objective optimization problem in the context of LCA can be formulated as given in Equations 3.1 and 3.2.

## 3.3. Combination of Process Synthesis & LCA

### *3.3.1. ECO-optimization*

In case of superstructure optimization applied in this work, all potential configurations of equipments (e.g. regenerators) of interest and the interconnections within the system are accounted for the initial superstructure with heuristics from experience. This initial superstructure promises to have the "best" solution alternative in its structural options and is integrated into a simultaneous mathematical optimization sequence, which provides an advantage of performing simultaneous optimization of the configuration and operating conditions (Grossmann, 1999).

To synthesize RRNs with reference to this superstructure material and compound balances, cost and energy equations and process requirements are developed in a mixed-integer nonlinear program (MINLP). In the mathematical model for ECO-Optimal Design Concept the environmental objective is provided by some phases of Life Cycle Assessment (LCA), which serve as a tool for decision-making and strategic planning (Burgess & Brennan, 2001). Throughout systematic analysis of process flow networks, it enables to calculate quantitative scores as indicator results (Ti). The economic objective is defined as a function of total annualized costs (TAC) considering investment and operational costs of each process unit in the network.

Due to incommensurability of these criteria, the quality of a solution can not be quantified. Instead a Pareto Optimal Solution Set[2] found within the given constrains provides a base for decision making among the solutions. In this work, a weighting method is applied to find a Pareto optimal solution, which allows the optimization of these criteria simultaneously (Sing, 1996). The weighting factors α (alpha) and β (beta) determine the relation between both objectives integrating in a single objective. In this work α- value is set to 1 [1/€] and β-values are determined by solver results in which an intuitive range sense is developed that gives an idea about where the range can be varied. This implies that the range of β is limited to $\beta = 0$ on one end, meaning minimum for TAC and $\beta \geq 0$, on the other end. This gives the minimum

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[2] A Solution X to a multiple objective problem is Pareto optimal if no other feasible solution is at least as good as X with respect to every objective and strictly better than X with respect to at least one objective (Sing,1996)

region of environmental relevance to the system. The upper limit for β can be ascertained by having both objectives in the same order of magnitude as in the main objective function.

### *3.3.2. Simultaneous Analysis of Environmental Impacts Sensitivity (SAEIS)*

As a systematic analysis method in this work, a simultaneous analysis of environmental impacts sensitivity (SAEIS) that is based on a procedure proposed by the authors (Erol & Thöming, 2005) is used. This is based on LCA and Life Cycle Inventory Analysis (LCIA), which provides the indicator values (Ti). Furthermore a relative increase score (Ti') is obtained by dividing (Ti) of RRN by the reference (Ti) of a standard system. In the case of a rinsing process this standard system is a Rinsing Network (RN) without recycling. By taking such a normalized (Ti') value for each indicator category, a dimensionless environmental relevance score is achieved. From this set of values the maximum relative increase score realized is used for a quantitative representation of environmental impact potential of the system.

In SAEIS analytical hierarchy process is not used in contrary to usual applications in multi-criteria methods, since instead of a generation and synthesis of priorities just a representation of decision maker's preferences is favored by attaining weights such as (α) and (β) to the objectives. The weighting method leads the decision maker to a deductive determination of the best alternative needed for the instance. The ecological criterion chosen as a representative by the max-selection of SAEIS algorithm reduced the number of various ecological objectives to an absolute number that can be meaningfully weighted. In this case, the absolute number, representing the ecological part of the multi-objective function, is traded-off with TAC.

Integration of both eco-eco trade-offs in the multi-objective function is done by means of the weighting method, which is used to generate Pareto optimal solutions (Proos et al, 2001). The set of Pareto optima for the problem is produced by varying the weighting on each eco-criterion, but in this case especially the weight (β) for ecological criteria is varied and the weight (α) is set to be constant. Thereby it enables the observation of the dependence of the process design on ecological criteria.

The indicators for each environmental impact category can be calculated with different environmental impact assessment methods. Currently the problem-oriented approach applied in this study is deemed the "best practice" for impact assessment (LCA, 2001). The problem-oriented approach with impact categories are defined at the mid-point level, which allows fewer errors by implementation.

### *3.3.3. SAEIS Method Combined with MINLP*

After taking all relative increases and selecting the maximum value (Ti'max) in the SAEIS, the environmental objective part of the multi-objective function, which enables the simultaneous trade-off between TAC and environmental relevance score of the network system, is derived. This multi-objective function is integrated into a mixed integer nonlinear programming algorithms for solving the rinsing recycling network. The schematic presentation of this method is to be seen in Figure 7.

Before performing a trade-off between objectives, the initialization in the model is done. This is to provide a better approach to the best solution-alternatives from many local optima. With some initial levels that are set for key parameters and some flow rates of concentrates, all the other variables are expressed as functions of the preceding ones. It should be noted that by varying these initializations different local optima alternatives can be produced.

In this SAEIS method, the LCIA is used for expressing the environmental objectives in figures. The required supplementary data for calculating the quantitative environmental indicator values is taken from a data set in LCA Guide of CML (LCA, 2001). The data set defines environmental impact categories (i) and conversion factors (CFi,s) for certain substances (s). The observed substances are quantified by material input-output balances of the system.

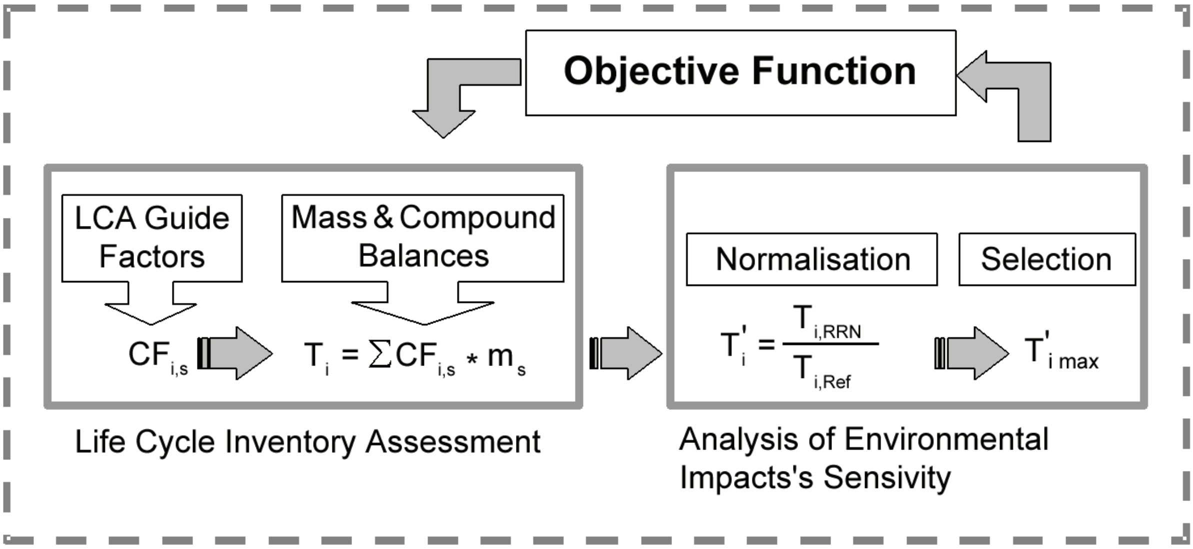

Figure 7: The core of the synthesis procedure. Simultaneous analysis of environmental impacts sensitivity SAEIS as a part of the MINLP (Erol & Thöming, 2005)

For the toxicity related environmental impact categories (HT: Human toxicity, FWST: Fresh Water Sediment Toxicity, FWAT: Fresh Water Aquatic Toxicity) in the wastewater and drag-out streams leaving baths, the concentration and flux of the toxic substances are considered. Depletion of resources (DAR) is described by amounts of bath chemicals, water consumption, and fossil energy resources. Additionally the energy's contribution to 'climate change (CC)' in terms of $CO_2$ emission is taken into account. As a result a quantitative representation of environmental impact potential of the system, the indicator values (Ti) are calculated.

To address the environmental improvements or worsening of regeneration and recycling in comparison to a system without recycling and reuse (reference system), a relative value (Ti´) is calculated, dividing the Ti values of a recycling system by reference values TRef,i. This normalization leads to a dimensionless relevance score Ti´.

Generally, normalization is done to obtain comparable scales either unitless or converted to common units (Norris, 2001). In LCA literature, normalization differs in two regarding their purposes. In the first instance, an operational requirement for valuation, which is the weighting of impact categories or their results, is defined and provides comparability (Consoli et al., 1993) of the data in form of a basis for the valuation step (Seppälä, 1999). In the second case, a function of "putting the characterization results in context" is defined as a method for "analysis of significance" (Barnthouse, 1998). This definition of normalization is interpreted in different works such as for better understanding the relative proportion or magnitude for each impact category of a system or for denoting the contribution of the characterization results to well-known environmental problems. In this way, the emphasis is given more for assessing the relative significance of the results over the other impact categories and showing the wider context of case-specific LCA results.

By taking such a normalized Ti´ value for each indicator category, a dimensionless environmental relevance score is achieved. From these Ti´ scores a representative maximum score (Ti´max), representing the quantity of strongest environmental impact potential of the system, is chosen. The use of a max function calls for discrete nonlinear programming (DNLP). Nevertheless, the used SBB solver of the software-package GAMS (21.3) cannot handle multi-objective mixed integer nonlinear programming (MINLP) and DNLP at the same time, max-function could only be used in initialization and the maximum approximation in model is done by n-Norm.

In this sequence, the representative Ti´max value is derived. This forms the environmental objective part of the multi-objective function, which will enable the ECO-trade-off between economical and ecological objectives by certain weighting ratios (β) simultaneously. These weighting ratios specify the relation between both trade-offs such as weakly weighted or equally weighted within the given constrains.

The SBB-solver routine used to solve MINLP algorithm combines the relaxed mixed integer nonlinear programming (RMINLP) reference solution with branch and bound method (BBM) and standard nonlinear programming (NLP) solvers for the submodels solved in each node of BBM.

After defining the MINLP superstructure, the variables will be initialized and the model will be solved for RMINLP problem. RMINLP is derived by interpretation of the integer variables in MINLP model as continuous variables. If all discrete variables in RMINLP are integers, then the solution reached is the optimal integer solution. If not, the BBM procedure over a binary tree, representing the combinations, will be started. The feasible region for discrete variables is partitioned into subdomains systematically and the bounds on these discrete variables are tightened to new integer values for cutting-off the current non-integer solution. At different levels of this enumeration, valid upper and lower bounds are generated. By tightening a bound, each time a tighter NLP submodel is solved starting from optimal solution to the previous looser submodel. This sequence is repeated in a loop for each node until there is not any branch with open node to solve left.

The SAEIS in this MINLP algorithm figures out the most sensitive indicator value and indicates the environmental relevance of the system in the multi-objective optimization problem. The overlapping of MINLP algorithm with SAEIS is shown in the schematic presentation in Figure 8.

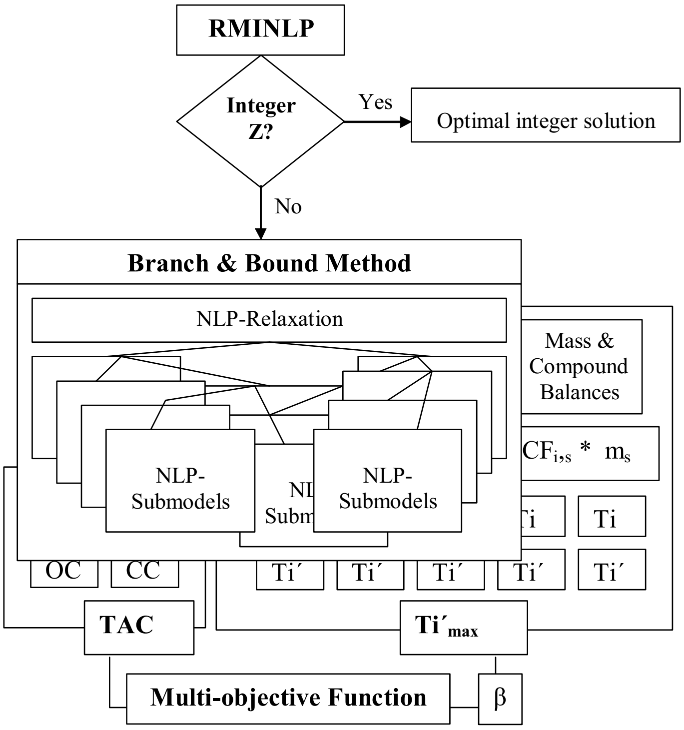

Figure 8: Schematic presentation of MINLP algorithm with SAEIS

TAC: Total annualized costs, OC: Operational cost, CC: Capital cost, β: Weighting factor, Ti´max: Representative relative indicator score for relevant impact category (i), Ti´: Environmental relevance score, Ti: Indicator values, ms: Mass of relevant substance (s), CFi,s: Conversion factor for relevant impact category (i) and substance (s)

# CHAPTER 4 – CASE STUDY MODELLING

Sustainable processes concept for metal finishing can be realized through improved environmental management with economic returns. Different approaches like process solution purification and recovery, rinse purification and concentrate recovery, implementation of alternative processes and coatings (substitution) and also retrofitting for existing processes pursue this sustainability concept.

Purification of metal finishing process solutions enables extended use of bath chemistries while reducing wastes and chemical purchases which is a gain of both ecological and economic aspects. Purifying and recycling of process rinse water besides reducing water use, also reduces wastewater generation and contaminant load from influent water. In some cases it is also possible to recover concentrated solutions during rinse water purification.

Process substitution is also a form of process optimization, where environmentally cleaner process alternatives replace existing processes in part or in whole. Process substitution, however, will not automatically result in cleaner manufacturing. In assessing alternative processes, the first step is to review existing processes for opportunities to optimize those processes.

All these tasks for process improvement in form of substitution or modifications to the existing ones need optimization sequences. Optimization in this case can either be a water network allocation problem with regeneration units and with an evaluative objective or an optimization of network with more detailed specific functional optimization of each unit.

A variety of optimization tools and regeneration technologies are available to enable surface finishing manufacturers to approach or achieve zero discharge in terms of sustainability (EPA, 2000). Individual or combined actions consisting of source reduction, process water recycling, and process substitution need to be considered to determine the best approach for specific applications. Understanding process chemistry and production impacts are essential to the identification, evaluation, and implementation of successful sustainability.

In this work nickel plating and phosphating with regeneration units are considered as case studies. The available regeneration technology for these specific cases were of electrodialysis (ED), reverse osmosis (RO), ion-exchanger (IX) for nickel plating and nanofiltration (NF) and reverse osmosis (RO) for phosphating. These are chosen mainly for purifying and recycling of process rinse water (Cushnie Jr., 1994).

Rinsing recycling network (RRN) design problem was handled with following considerations: Operation units for water usage and treatment, contaminants and freshwater sources are determined. Then, all possible network connections are introduced with mixing and splitting points (Alva-Argaez et al., 1998). Prior to each operation a mixer and behind each operation a splitter are placed (see in Figure 6). Fresh water and drag-outs entering the network is split towards all operations and corresponding effluent streams generated from each operation are mixed and brought up to a final discharge point, where environmental limitations are to be hold.

For the mathematical formulation mass and compound balances are defined for every contaminant around each operation, mixing and splitting unit. Binary variables are introduced for each possible connection. Removal ratios, fixed type of recycling and regeneration units and flow rate limitations are taken as assumptions. In stead of integrating detailed models of each operation unit into the whole network model some constant ratios are used just to simplify for observing other features in multi-objective optimization sequences such as economic aspects versus ecological aspects.

Eco-optimization method with a systematic analysis called SAEIS is applicable for any kind of process where environmental and economic aspects are to be traded-off. After determining the superstructure: process flows and units that are necessary, the contaminant within the network and corresponding indicators for their environmental burden potentials, the core SAEIS algorithm can be employed in a multi-objective optimization sequence.

Depending on the goal of the study to illustrate the ECO-optimised process alternatives the below given metal finishing case studies are considered. In these cases besides generating ECO-optima, comparison of closed-loop and open-loop systems, dilemma of environmental aspects in recycling networks and the compromise between objectives are examined.

## 4.1 Case Study I: Nickel Plating

To work out the ECO-design of metal finishing plants by means of multi-objective optimization of economic and environmental aspects a large scale nickel plating process including rinsing stages is selected as first case study. This process was previously defined as a closed-loop system for zero-water discharge (Thöming, 2002) with the closed-loop conditions $W = \mathbf{0}$ and $D = C$ (see in Figure 9). Total annual costs were minimized for different rinsing criteria (RC). The local optima received by means of a single objective MINLP provide different network alternatives.

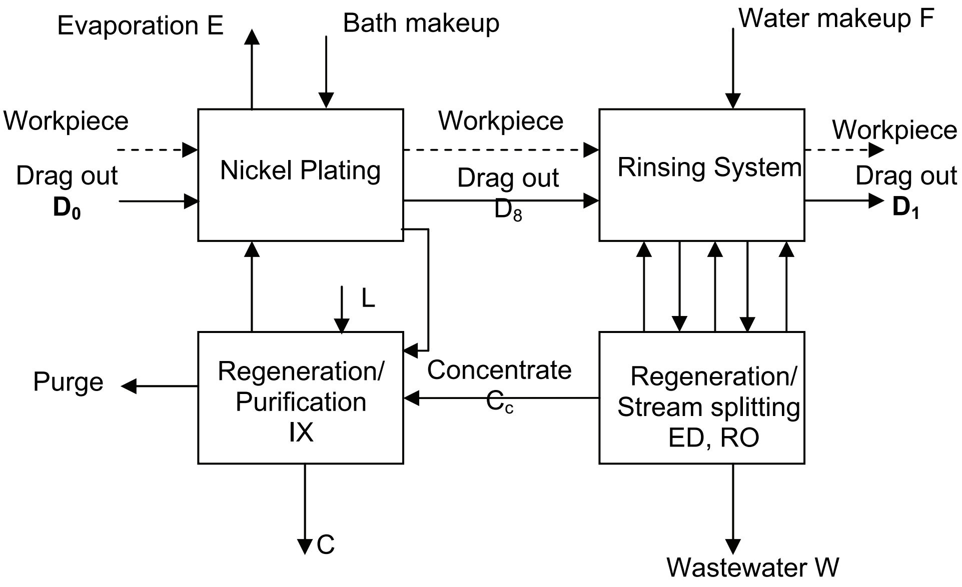

Figure 9: The structure of the investigated open-loop nickel plating process
ED: Electrodialysis; RO: Reverse osmosis; IX: Ion-exchanger (Erol & Thöming, 2005)

In this work the structural representation of the zero-water discharge rinsing and recycling network (RRN) is converted into an open-loop RRN with some open-loop conditions such as

$$F \geq D + E \text{ or} \tag{4.1}$$

$$F = E + W \qquad W \geq 0 \tag{4.2}$$

$$C_c = E \tag{4.3}$$

and heuristic rules. The water make up is restricted to the final rinsing stage used in closed-loop model, two more heuristic rules are included for the open-loop model, they are the amount of concentrate which is recycled and substitutes the drag-out.

Extending the closed-loop model to this open-loop model, the potential environmental impacts of a wastewater discharge can be seen. In this case study the following environmental impacts were considered: the amount of nickel in wastewater stream, the water consumption of the system and the energy consumption for pumping and regenerator units. The mathematical expressions of the mentioned environmental impacts and their inclusion into the model are to be seen in the Appendix-I.

As electrolyte the plating bath contains Watt's nickel solution. The nickel ions are classified as reproductive toxicants and as category 3 carcinogen (Anonymous 2, 2003). These effects, the environmental impact categories human toxicity, fresh water aquatic toxicity, and fresh water sediment toxicity are to be examined in the environmental impact assessment of the nickel plating.

Besides the potential environmental impacts of hazardous substances, the increasing depletion of resources is considered. The fresh water consumption and the energy resources to run the RRN are considered under the category of depletion of abiotic resources.

### *4.1.1. Structural Representation of Open-loop Rinsing and Recycling Network (RRN)*

In Figure 9 the structure of a nickel plating step is presented. The nickel plating bath is typically followed by a rinsing system, combined with regeneration units for different purposes such as bath make up, bath solution recovery and rinse water reuse.

In order to define the detailed material balances through the system, RRN is examined separately from the process bath by means of the superstructure in Figure 10. In this superstructure the stream interconnections within the RRN that define all possible configurations including regeneration, stream splitting, recycle of dilute and concentrate solution, stream mixing, and bypass streams are represented.

The RRN shown in Figure 10 consists of eight counter-current rinsing stages, which are combined with regeneration system, comprising reverse osmosis (RO), electrodialysis (ED) and ion-exchange (IX) and all possible interconnections between each unit.

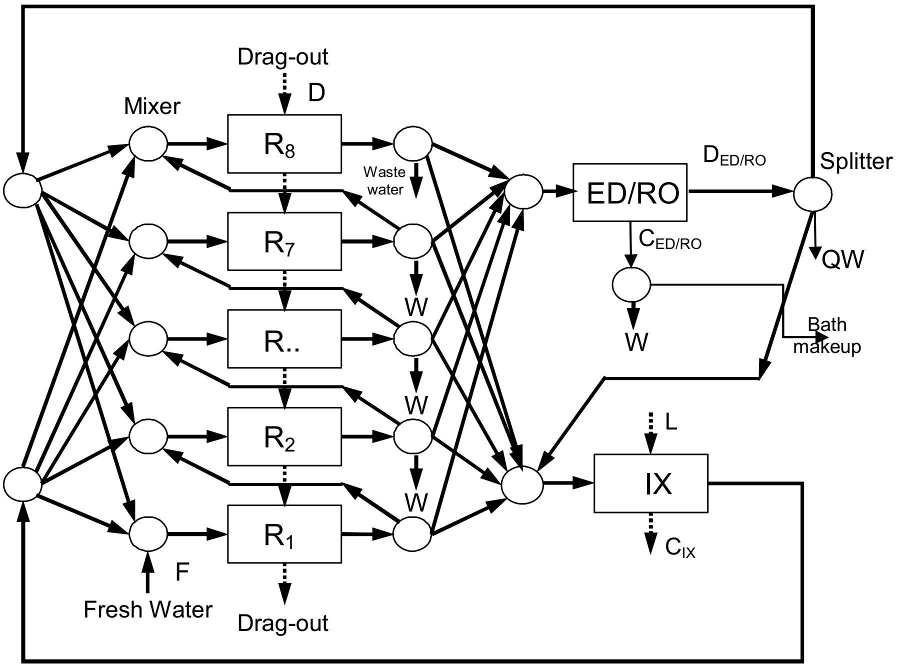

Figure 10: Superstructure of RRN for the nickel plating case study. R: Rinsing stage; ED: Electrodialysis; RO: Reverse osmosis; IX: Ion-exchanger (Erol & Thöming, 2005)

### *4.1.2. Structural Representation of Standard case Rinsing System (RS)*

The standard case rinsing system, is a basic rinsing system without any reuse and regenerator units. It discharges the wastewater produced in the system after three stages of rinsing to the environment or a treatment facility not considered in this case (see in Figure 11). It can be taken as a worst-case reference of a rinsing system and provides a comparison basis between the potential impacts of a standard rinsing and a reuse – recycling system.

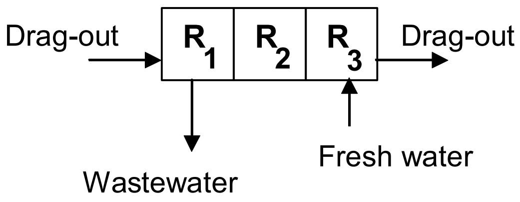

Figure 11: The structure of standard case rinsing system (Erol & Thöming, 2005)

The standard case also functions as a normalisation basis in the simultaneous analysis of environmental impacts sensitivity (SAEIS). This is in order to get to an environmental relevance score for the system without units.

In this case study, the multi-objective function describes two incommensurable objectives. They are total annual cost (TAC) and relative increase of the environmental impacts of RRN to the standard case RN, which enable the determination of the relation between both economic and environmental aspects of RRN as a function of trade-off parameters. These trade-off parameters are flow rates and concentrations. The mathematical expressions for both RRN and standard case RN models are given in details in the Appendix-I.

### 4.2. Case Study II: Phosphating

The ECO-optimal design of phosphating process including the rinsing system is proposed by means of multi-objective optimization of economic and environmental aspects. The economic aspects in terms of mathematical expressions are declared as correlated capital and operational costs, which are taken from a reference data set given for evaluation in Wright & Woods (1993); Wright & Woods (1995). Under environmental aspects the impact of the amount of nickel, zinc and manganese in wastewater stream, the water consumption of the system and the energy consumption for pumping and regenerator units and chemical consumption for $Me^{2+}$-precipitation are considered.

Superstructure in Figure 12 consists of a phosphating bath, from which the drag-out (D) enters the rinsing stages up to 8 $R_1$ to $R_8$, the outlet of the rich stream is divided into sub-streams. These sub-streams are received by regenerators, nanofiltration (NF) and reverse osmosis (RO) for reuse. By means of nanofiltration concentrate produced for reuse in the phosphating bath, recycling of nickel and other bath chemicals is realized. Additionally, disturbing compounds, like decomposed accelerators, must not be retained. Due to those compounds, the permeate is of moderate quality with respect to rinsing water reuse. To produce recycle water of higher purity, RO can be used additionally. The embedment of all potential configurations of interest and the interconnections within the system are done by ascertaining mixers, where the streams gather and splitter, where the streams are divided into sub-streams.

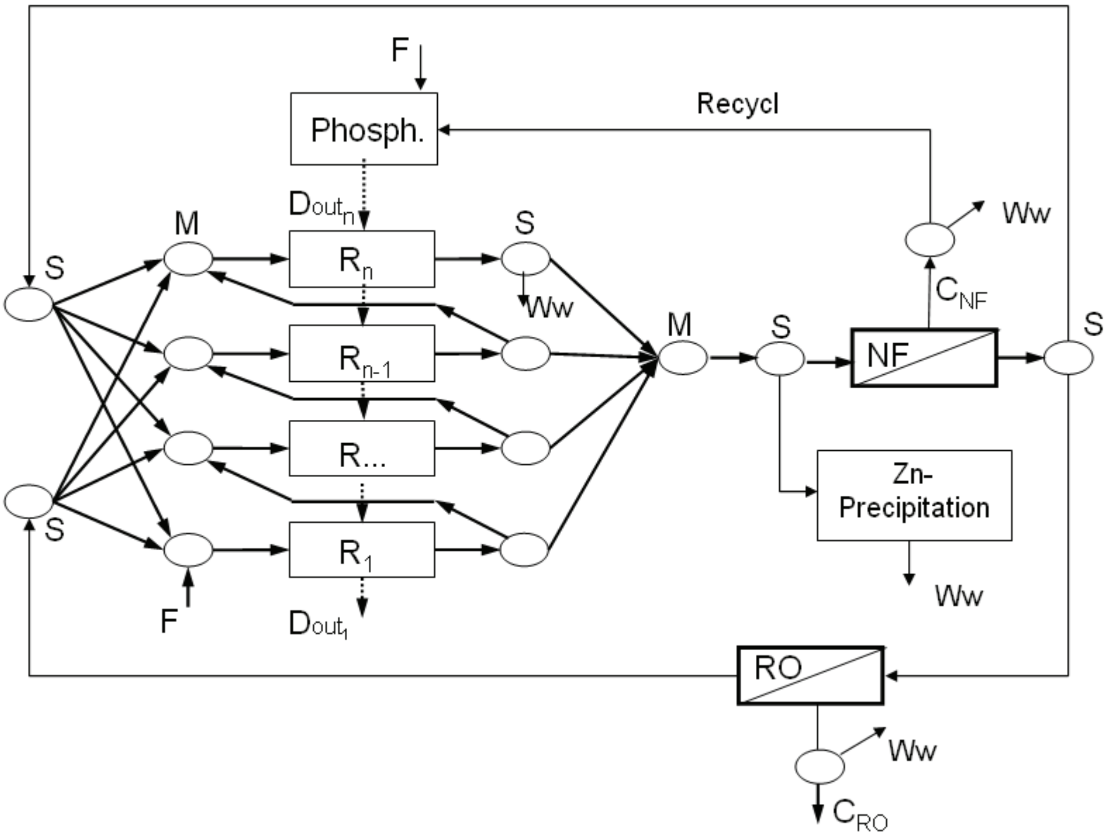

Figure 12: The superstructure of RRN for phosphating in metal finishing. D: drag-out, FR: fresh water inflow, M: mixer, NF: nanofiltration, R: rinsing stages, RO: reverse osmosis, S: splitter. (Erol & Thöming, 2006)

To easily handle the complex model, a classification into rinsing, concentrators, effluent treatment, mass, energy, eco and cost modules is carried out. Each physical content is described by mass, compound and energy balances. The basic modules as rinsing, concentrators, effluent treatment and bath are given in Appendix-II. The modules that enlighten the ECO-optimization model are as follows:

**Energy module:** Pumping energy for freshwater inflow $E_F$ is calculated over a year by attaining the specific work (spezW) for centrifugal piston pump in kJ/kg, flow rate of the streams in kg/h with a conversion factor of 0.28 from kJ to Wh and a conversion factor of 8000 h/a as a mean value of working hours in a year:

$$E_F = 0.28 \, . \, \text{spezW} \, . \, (F_R + F_{Bath}) \, . \, 8000 \quad (4.4)$$

Absolute power requirement for pumping is determined by considering the efficiencies of the pump $\eta_p$ 90 % and motor $\eta_m$ 70%:

$$Ep = \frac{\text{Ef}}{\eta_p \eta_m} \quad (4.5)$$

Energy consumption of concentrators $E^J$ is estimated by the specific work spez$E^J$ needed per dilute stream flow of each concentrator regarding the assumptions in Perry & Green (1997).

$$E^J = Q_D^J \, \text{spez} \, E^J \ \text{x} \ 8000 \quad \forall \, J \quad (4.6)$$

The total amount of energy utilization is ascertained by the sum of pumping and concentrator units' energy consumption:

$$E_{tot} = \text{Ep} + \sum_{j \in J} E^J \quad (4.7)$$

Mathematical expression for total annualized cost function consists of operational costs OC and capital costs CC for each unit in the RRN structure. The cost projection assumptions for operational and investment costs are taken from Wright & Woods (1993); Wright & Woods, (1995) and specific regenerator properties from Perry & Green (1997).

$$TAC = \frac{\text{OC} + \text{CC}^{\text{NF}} + \text{CC}^{\text{RO}} + \text{CC}_{\text{R}} + \text{CC}_{\text{ZnP}}}{a} \quad (4.8)$$

The operational costs OC depend on the flow rate per unit, the number of used units, the amount of trace elements and energy used, where the cost of the energy for the concentrators are already integrated into the costs per flow rate. These costs are annualized by the conversion factor 8000 h/a. Therefore we get

$$OC = \sum_{j \in J} CC^j \; Q_D^j + CC_R \cdot \sum_{j \in I} Q^i \text{ x } 8000 + \sum_{t \in TE} C_t \; MIND^t + C_{WW} \; Q_{Wtot} \text{ x } 8000 + C_{EN} \frac{E_f}{\eta_p \eta_m} \tag{4.9}$$

The capital costs CC are calculated by means of correlations recommended in Wright & Woods (1993), using an exponent $IC_p$ for RO, NF, ZnP and the reference values of costs and flow rates defined for this correlation. The $CC_s$ for units RO, NF and ZnP are given by:

$$CC^{RO} = IC_{RO} \left( \frac{Q_D^{RO}}{16700} \right)^{IC_{RO}^P} \tag{4.10}$$

$$CC^{NF} = IC_{NF} \left( \frac{Q_D^{NF}}{16700} \right)^{IC_{NF}^P} \tag{4.11}$$

$$CC_{ZnP} = IC_{ZnP} \left( \frac{Q_{W,out}}{5700} \right)^{IC_{ZnP}^p} \tag{4.12}$$

For Rinsing units the reference cost parameter $IC_R$ per rinsing unit is taken from Thöming (2002) and $CC_R$ is calculated as follows:

$$CC_R = IC_R \sum_{i \in I} Z^i \tag{4.13}$$

**ECO Module:**

For attaining the environmental objectives in figures the amounts of the substances with potential environmental impacts are assessed by means of the supplementary data given in LCA (2001). This data set defines environmental impact categories c and conversion factors

CF for certain substancess. By means of these figures, the amount (mass indexes from mass balances) of potential environmental impacts can be converted into indicator values over a certain time horizon.

Mass Index (MIND) for the substances Ni, Zn, $CaOH_2$ and $H_2O$ are defined as follows:

$$MIND^{Ni} = \frac{(\mathrm{Y}_0^{\mathrm{Ni}} - \mathrm{X}_{out}^{1,\mathrm{Ni}}\ \mathrm{D} - \mathrm{X}_C^{\mathrm{NF,Ni}}\ \mathrm{Q}_{\mathrm{Recyel}}^{\mathrm{NF}}}{1000} = 8000 \tag{4.14}$$

$$MIND^{Zn} = \frac{\mathrm{Q}_{\mathrm{W,out}}\ X_{W,out}^{Zn}}{1000}\ \mathrm{x}\ 8000 \tag{4.15}$$

$$MIND^{CaOH_2} = \frac{\mathrm{X}_{\mathrm{M}}^{\mathrm{Zn}}\ Mwt^{CaOH_2}}{1000}\ \mathrm{x}\ 8000 \tag{4.16}$$

$$MIND^{Wa} = (\mathrm{F}_{\mathrm{R}} + \mathrm{F}_{\mathrm{Bath}})\ \mathrm{x}\ 1\ \mathrm{x}\ 8000 \tag{4.17}$$

The amount of resources consumed for total energy consumption within the system is calculated considering the country's specific distribution % of energy resources utilization for generating electricity and the related efficiency of the power station technology applied. Its contribution to $CO_2$ emissions is assessed by means of $CO_2$ emission's factor (kt/PJ) defined in Lichtblick (2002).

Mass index for energy resources which are soft coal SC, hard coal HC, natural gas NG and crude oil CO:

$$MIND^S = \mathrm{E}_{\mathrm{tot}} \frac{FRAC^S}{0{,}28\ \mathrm{x}\ 10^3\ \mathrm{x}\ \mathrm{h}^{\mathrm{s}} WG^S}\quad \forall\ \mathrm{s} \tag{4.18}$$

Where $E_{tot}$ is the total amount of energy used in kWh, Frac is the fraction of energy from the energy mixture of Germany in 2002, that is provided by energy resource s, $h_s$ is the heating value MJ/m$^3$ of s per kg, $WG_s$ is the efficiency of energy production using s and f is a conversion factor which converts MJ to kWh.

Environmental Impact Indicator value $IND_{c,s}$ for each indicator category related with considered substance:

$$IND^{C,S} = \mathrm{CF}^{\mathrm{C,S}}\ \mathrm{MIND}^{\mathrm{S}} \quad \forall \mathrm{c,s} \tag{4.19}$$

C is the set of considered impact categories: C = human toxicity, fresh water aquatic toxicity, fresh water sediment, depletion of abiotic resources.

The $T_i$ value for each impact category is:

$$T_i^C = \sum_{\mathrm{s}\in\mathrm{S}} IND^{C,S} \quad \forall \mathrm{c} \tag{4.20}$$

The relative value of environmental impact indicator for each indicator category is:

$$T_{i,\mathrm{Rel}}^C = \frac{\mathrm{T}_\mathrm{i}^\mathrm{C}}{\mathrm{T}_{\mathrm{i,\,Ref}}^\mathrm{C}} \quad \forall \mathrm{c} \tag{4.21}$$

The maximal relative value $T_{i,Rel,\ max}$ of environmental impact indicator out of all indicator category is:

$$T_{i,\,\mathrm{Rel,\,Max}} = \max_{\mathrm{c}\in\mathrm{C}} \left(\mathrm{T}_{\mathrm{i,\,Rel}}^\mathrm{C}\right) \tag{4.22}$$

Multi-objective function (ZF) which integrates both eco-eco trade-off in a function is:

$$ZF = \alpha\, \mathrm{TAC} + \beta\, \mathrm{T}_{\mathrm{i,\,Rel,\,max}} \tag{4.23}$$

The minimization of the objective function ZF that is subject to the constraints which form the feasibility region is referred to a mixed-integer nonlinear program (MINLP). This is due to the non-linearity of Equations AII-3, AII-9, AII-10, AII-22, AII-23, AII-29, AII-30 and the binaries in the Equations AII-6, AII-7, AII-13 and AII-28.

The optimization problem here is to achieve an eco-optimal system structure, which comprises an optimal number of rinsing stages and an optimal arrangement of regenerators controlled with corresponding economic and ecological aspects. This integration of these eco-eco trade-offs in terms of TAC and Ti'max in a multi-objective function is represented in Eq. 2.20. The representative objectives in the objective function are outcomes of (a) mass and compound balances for compounds with potential environmental impacts (Eqs. AII-1 to AII-38, Eqs. 4.4 to 4.7 and Eqs. 4.14 to 4.22), (b) the regenerator and rinsing unit specifications, like specific costs (Eq. AII-5 and Eqs. 4.8 to 4.13) and regenerator performances (Eqs. AII-15, AII-18 and AII-25) and (c) system parameterizations like flow rates of recycle streams. All these influences are represented in the case study by the equality constraints (Eqs. AII-1 to AII-5, AII-8 to AII-12, AII-14, AII-15, AII-17 to AII-20, AII-22 to AII-27, AII-29 to AII-38) and by inequality constraints (Eqs. AII-6, AII-13, AII-16, AII-21 and AII-28). The existence of the units is controlled by binary variables AII-7 and by flow rate limitation inequality AII-16.

In mathematical programming, all system variables in optimization models should be properly initialized to achieve reasonable solutions. If not, MINLP problem is usually difficult to solve, since then it results in a discrete optimization problem (Grossmann & Kravanja, 1995). For example in this case study, when the max function is applied at initialization and n-Norm is used in model algorithm at the same time, the most sensitive indicator value differs from the value calculated by n-Norm, if $T_{i,Rel,\ max}$ value is $0 < T_{i,Rel,\ max} < 1$. This happens due to the contrary requirements of MINLP and DNLP.

The solution of the MINLP, modelled in GAMS, version 21.3 (GAMS, 2004) using the SBB solver, provides the unit interconnections, the flow rates and concentration of each stream in the superstructure and the number of rinsing stages.

# CHAPTER 5 – CASE STUDY RESULTS AND DISCUSSION

Higher compatibility of a system needs environmental and economic assessment of the systems. The recycling systems with an optimal process structure are actually not fully operating with a closed loop. Therefore a challenge for identifying an open-loop RRN is investigated. The eco-optimal design alternatives are evaluated to outline the compromise between environmental and economic performance on a non-inferior surface.

Multi-objective optimization methods offer a wide range for decision-making, since the solution set of multi-objective optimization offers a set of alternative options for system improvements rather than a single prescriptive solution without excessive costs. After analysing all trade-offs among objectives, the best compromise solution can be chosen from the set of optimal solutions on the non-inferior curve. In this sense multi-objective optimization methods provide information on the trade-offs between different conflicting objectives showing what to be gained or what to be lost by choosing an alternative. If all objectives are equal of importance, then choosing the best compromise solution can be made by identifying the operating conditions. The integration of LCIA phase of LCA in multi-objective optimization enables quantitative scores for environmental objectives which leads to eco-eco trade-off , so called eco-optimization.

In this work mixed-integer non-linear programs (MINLP) are deployed for trading-off the environmental impact and total annualized costs simultaneously. The eco-optimal design alternatives are produced by the sensitivity based quantitative comparison between ecological and economic aspects which leads to the most sensitive environmental impact category for the system and integrates into a multi-objective optimization problem. The applicability of the proposed method has been described and demonstrated in case studies of synthesis of a nickel plating and a phosphating-rinsing lines in metal finishing.

The solution set of multi-objective optimization provides a set of alternative options for system improvements rather than a single prescriptive solution, thus enabling the choice of the best practicable environmental option without excessive costs

## 5.1. Nickel Plating Case

A multi-objective optimization results to a Pareto optimum. That does not mean that each objective has its own global optimum as they are not optimized individually. There is no guarantee to reach a global optimum because of the non-convexity of the problem.

In all calculations of the Pareto set of solutions there are two steps followed: in the first step the calculation was carried out at an assumed rinsing criterion (RC) with different beta values. Then in the second step, observing the tendency of Pareto Surface, some beta values are fixed. At these explicit betas, the solution-alternatives are derived. The optima for different RC values like 1000 and 50000 are obtained at varying β values between 1200 and 8400.

The set of local optima is illustrated in Figure 13 and Figure 14. Each optimum is characterized by a specific structural solution, here indicated by the number of rinsing stages, and different process parameters like flow rates and concentrations.

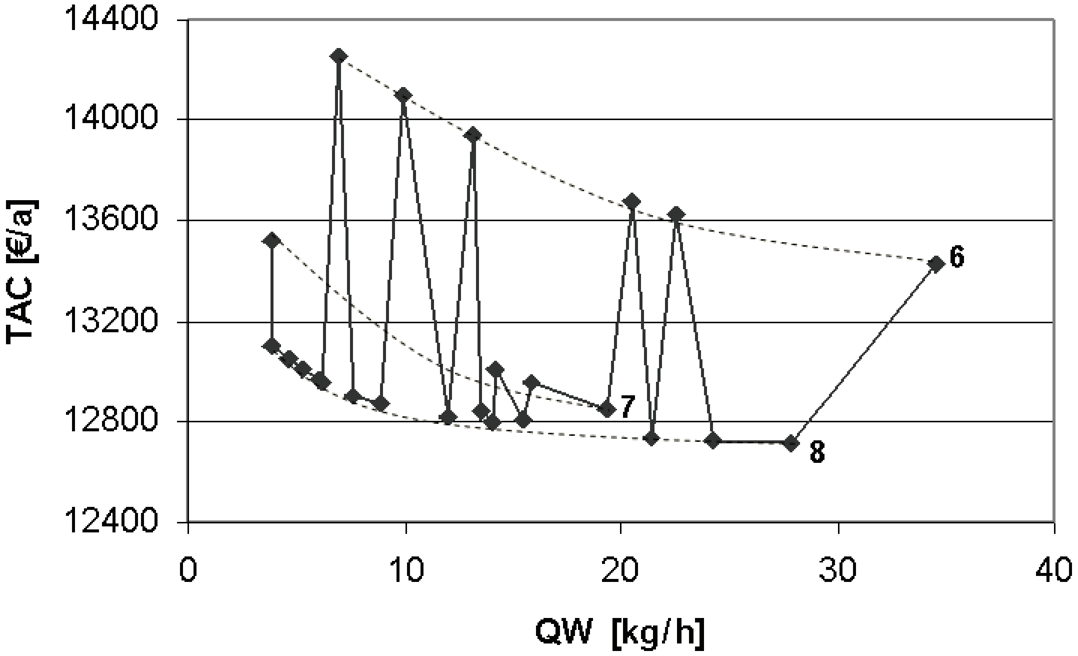

Figure 13: The set of local optima for a rinsing criterion of 50000. Total annualized costs (TAC) versus total amount of wastewater (QW) for different β values. The dashed lines indicate the number of rinsing stages as results of structural solutions. (Erol & Thöming, 2005)

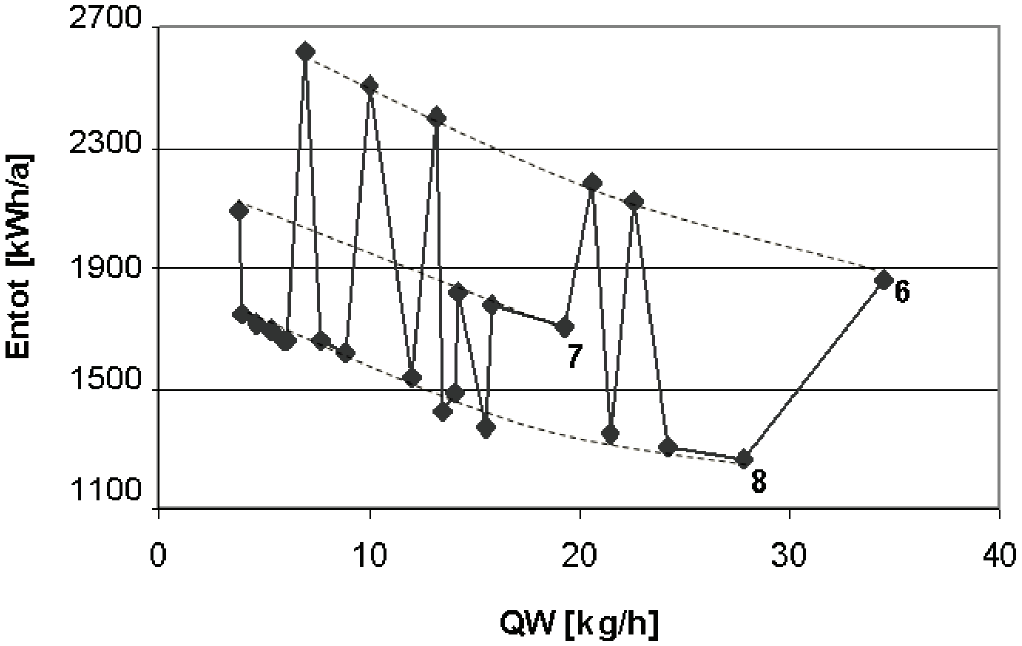

Figure 14: Total amount of energy consumption versus total amount of wastewater for different β values. The dashed lines indicate the number of rinsing stages as results of structural solutions. (Erol & Thöming, 2005)

As the system is forced to produce less wastewater, meaning less emissions or depletion of resources, the solutions reached with more rinsing stages cost less than systems with additional regenerators. The latter has an inherent 20-50 % more energy consumption. The zero-water discharge (QW=0) can be achieved with approximately 10 % increase of energy consumption in comparison to the open-loop RRN alternatives. Figure 14 shows that the high energy demand of regenerators and pumping have a great effect on costs and it also show mutual changes in energy consumption to other environmental impact categories.

The graphical representation in Figure 15 illustrates the tendency between both objectives TAC and the total amount of wastewater (QWtot) within the non-inferior set of solution-alternatives for a fixed RC. The total amount of wastewater represents the water consumption and toxic emissions as environmental impacts except energy, because energy consumption and the other environmental impacts have mutual behaviour to each other. The corresponding total annualized costs (TAC) of the solution-alternatives are also shown.

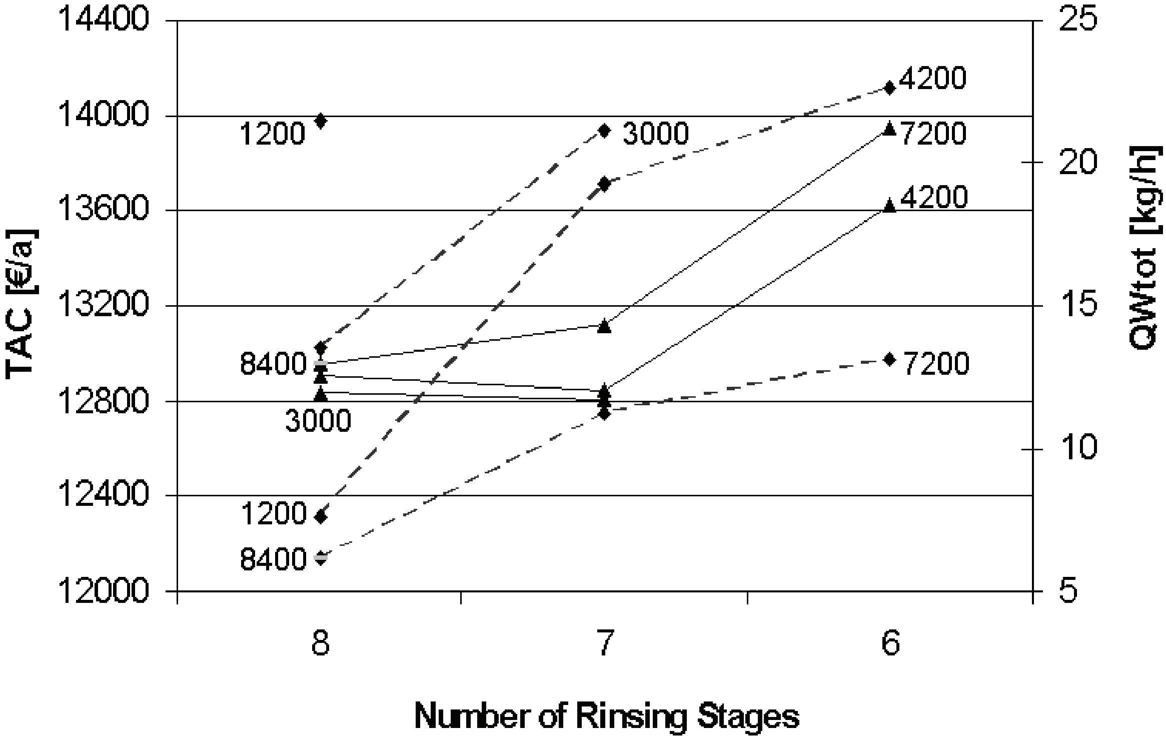

Figure 15: Total annualized costs (TAC) versus total amount of wastewater (QWtot) for different β values (RC=50000). The number of rinsing stages results from the optimization procedure and characterizes each local optimum. Straight lines indicate TAC, dashed lines the total amount of wastewater (QWtot) produced. (Erol & Thöming, 2005)

This set of solution-alternatives was derived using the procedures described above for calculation of the Pareto set of solutions. At a selected RC=50000, the results show that, as the β values increase from 1200 to 8400 (higher ranking of environmental impacts), there is a tendency for having a higher number of rinsing stages i.e. 7 or 8. The optimum obtained at β=7200 and β=4200 implies 8 rinsing stages and 7 rinsing stages respectively. All the solutions have reverse osmosis (RO) as a regenerator and additionally an ion-exchange (IX) regenerator. The structural presentation of the open-loop global optima shows a similar configuration to the closed-loop optima Thöming, 2002. Since IX is connected to the initial rinsing stages and the RO receives the rich stream from the last stages and provides regenerated stream to the third or forth rinsing stages in the middle.

In Figure 16 the effect of the RC on the objectives is shown. For RC=50000 optimum of both objectives is at 8 or even more stages. For RC=1000 economic optimum at 7 stages shows comparatively high environmental costs, so 8 rinsing stages appears to be the best compromise. The solution set at β=7200 with different RC 1000 and 50000 is illustrated in Figure 126. With an increase of RC from 1000 to 50000 at the fixed β=7200, the optimum design requires 8 fold rinsing at TAC=12953 €/a (RC=50000) instead of 7 rinsing stages at TAC=11702 €/a (RC=1000). It means independent of rinsing criteria there is a tendency for more rinsing stages. In case of RC=50000 approximately a 50 % reduction of the wastewater amount can be provided in stead of applying an extra regenerator which causes hidden wastes.

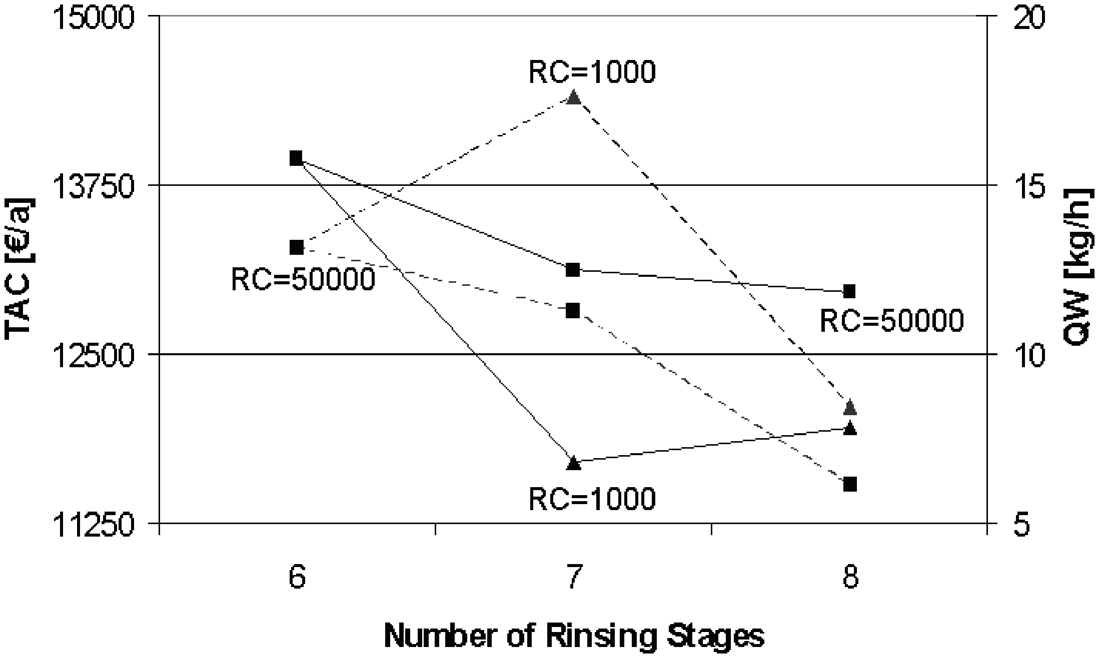

Figure 16: Total annualized costs (TAC) versus total amount of wastewater (QW) for different RC values with β=7200. Straight lines indicate TAC, dashed lines the total amount of wastewater (QW) produced. (Erol & Thöming, 2005)

The results of RRN that are produced under the open-loop condition show a comparable same tendency as the closed-loop results calculated by Thoeming2002. The highest TAC values are reached by fewer rinsing stages and with either RO or RO, IX.  Open-loop TAC values reach their minima at 7 or 8 rinsing stages.

They however differ with the regenerator used or rinsing criteria (RC) given as compared to the optima reached by closed-loop at 6 or 7 rinsing stages. The open-loop reaches optima with approximately 6 % lower TAC compared to the closed-loop solutions but with some wastewater discharge. Compared to closed-loop systems this purge avoids the problem of accumulating impurities.

Comparing open-loop alternatives with the standard case by TAC=462370 €/a, there is a reasonable saving potential to be seen by applying a reuse and recycling network in stead of standard case rinsing. Although the 70 % less energy consumption with 329 kWh/a makes standard case seem to be an environmental benign alternative, the environmental aspects causing the maximum possible burdens seem controversial.

The TAC decrease with increasing wastewater discharge indicates that, the lower the wastewater discharge is aimed, the higher the corresponding costs become. In this instance the system tries to achieve the same key parameter concentration with fewer rinsing stages, it is more costly since it applies more regenerators or high performance regenerators to achieve this target. The consequences are hidden wastes and economic discharges in form of energy consumption. To avoid this draw back the TAC minima can be preferably achieved through applying higher number of rinsing stages than an extra regenerator.

Pareto Surface/Front identifies a set of best possible options, in which both cost and environmental objectives should be improved. But on the Pareto Surface there is always a worsening or counter relation to an improvement in the other objectives. Therefore, there is a need for some trade-offs to get the preferred optimum solution within certain conditions. Considering a graphical representation of the non-inferior set and weighting the environmental relevance against economic objectives, the best compromised solution can be chosen based on the trade-offs.

In this metal finishing case study, applying the ECO-design by multi-objective optimization combined with LCA-tool as a hybrid approach, different RRN alternatives were received by varying the weighting factor for the representative impact score and the cost in the objective function. A replacement of either the standard or closed-loop systems by the discussed open-loop system, will result to the most environmental benign alternatives and with a reasonable return from investment.

## 5.2. Phosphating Case

In the ECO-process optimization model for this case study, the minimum number of initial values needed is four as given in Table 1 below.

Table 1: Initial and final values for each TAC and $T_{i,Rel,max}$ minimum

| | **Min.** | **β** | **$z^i$** | **$z^{RO}$** | **TAC ($10^3$ €/a)** | **$T_{i,Rel,max}$ (kg/h)** | **$Q^i_W$ (kg/h)** | **$Q^j_{WC}$ (kg/h)** | **$Q^j_{WD}$ (kg/h)** | **$Q^j_{Recycl}$ (kg/h)** | **$Q^{i,j}_{SP}$ (kg/h)** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Initial | | | 0.01 | 0.5 | | | 100 | | | 100 | | |
| Final | | | | | | | | | | | | |
| Case I | TAC | $10^5$ | 8 | 0 | 144.1 | 0.208 | 152 | 0 | 768 | 768 | 1536 | R8 → NF |
| | $T_{i,Rel,max}$ | $10^7$ | 8 | 1 | 153.7 | 0.142 | 152 | 233 | 0 | 768 | 1536 | R8 → NF |
| Case II | TAC | $10^5$ | 5 | 0 | 233.9 | 0.521 | 1337 | 0 | 768 | 768 | 1536 | R5 → NF |
| | $T_{i,Rel,max}$ | $10^7$ | 10 | 1 | 301.6 | 0.121 | 0 | 215 | 0 | 709 | 1418 | R10 → NF |

These initializations are the binary and positive variables for the existence of rinsing stages and regenerators. Starting from these initial values the rest of the model variables are calculated in sequence using the model equations as defined in Appendix-II and Section 4.2.

Depending on the weighting ratio β that relates the representative impact factor and the cost in the objective function different eco-optimal solutions of RRN alternatives are calculated and assessed. The absolute numbers for the weight (β) starting from 0 to $10^8$ are constituted so that both objective values are approximately of the same magnitude, which in Miettinen (2002) is said to be a demand/requirement of weighting method in multi-objective optimization. Scanning the whole range for the weight (β) that is in GAMS-solver available, the most sensitive values are ascertained. Smaller values do not supply different structural solutions, so the weight (β) values $10^5$ and $10^7$ are chosen to define a scale. The Pareto Front in Figure 17 that is produced with significant β-values ($\beta=10^5$ and $\beta=10^7$) demonstrate optimal process alternatives.

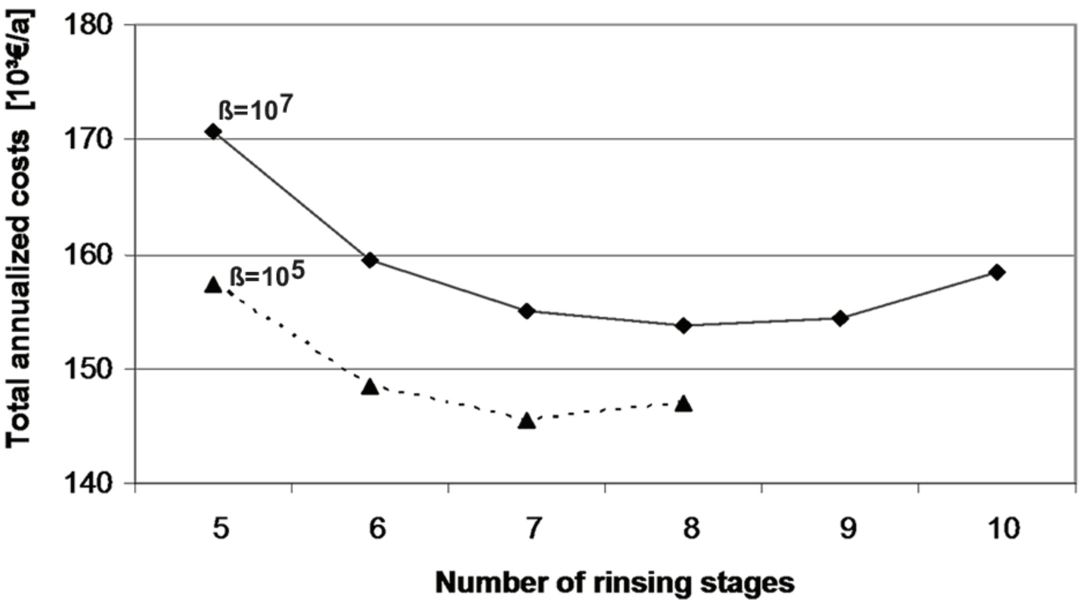

Figure 17: TAC versus number of rinsing (case I)

The global optimum of these different eco-optimal solutions of RRN alternatives are identified and assessed from this Pareto Front. The structural flow diagrams of each global optimum for significant β-values are as shown in Figure 18 and Figure 19.

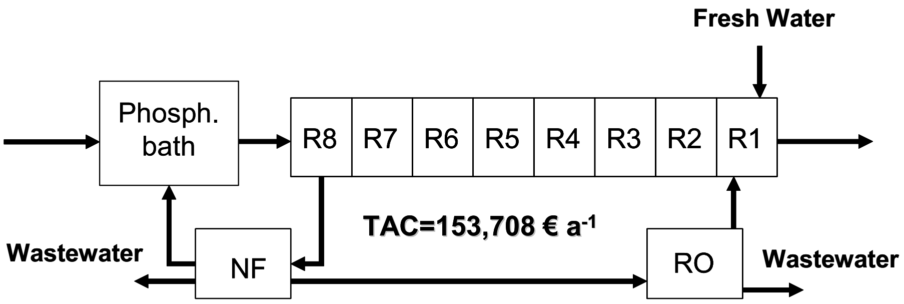

Figure 18: Structural flow diagram for global optimum RRN for $\beta=10^7$

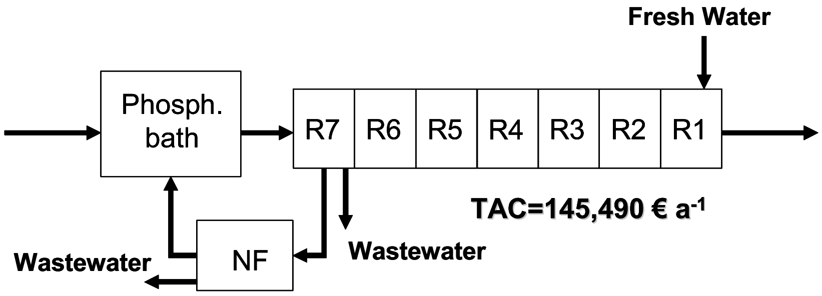

Figure 19: Structural flow diagram for global optimum RRN for $\beta=10^5$

For lower β-values the tendecy to produce wastewater is greater than to recycle the rich streams. The lower the wastewater discharge is aimed, the higher the corresponding costs become, since the system tries to achieve same discharge concentrations with additional rinsing stages and regenerators.

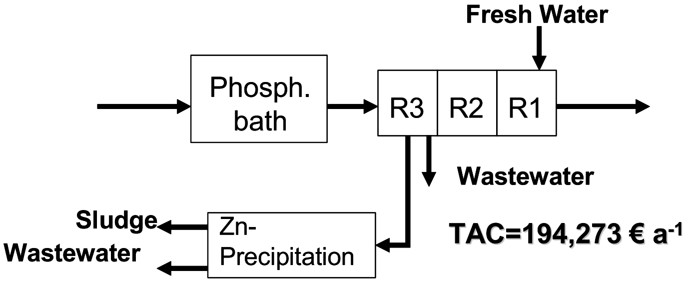

Figure 20: Structural flow diagram for the standard-case

The β=0 represents no environmental aspects considered, the β=$10^5$ represents weaker weighted environmental objective and the β=$10^7$ represents equally weighted economic and ecological aspects to attain the same order of magnitude between both objectives. On the Pareto Front of optimal solution set shown in Figure 21 the locals as well as the global optimum are illustrated for two β-values (β=$10^5$ and β=$10^7$) and two rinsing systems, a spray rinsing (case I) and an immersion rinsing process (case II) for which triple invest cost were given.

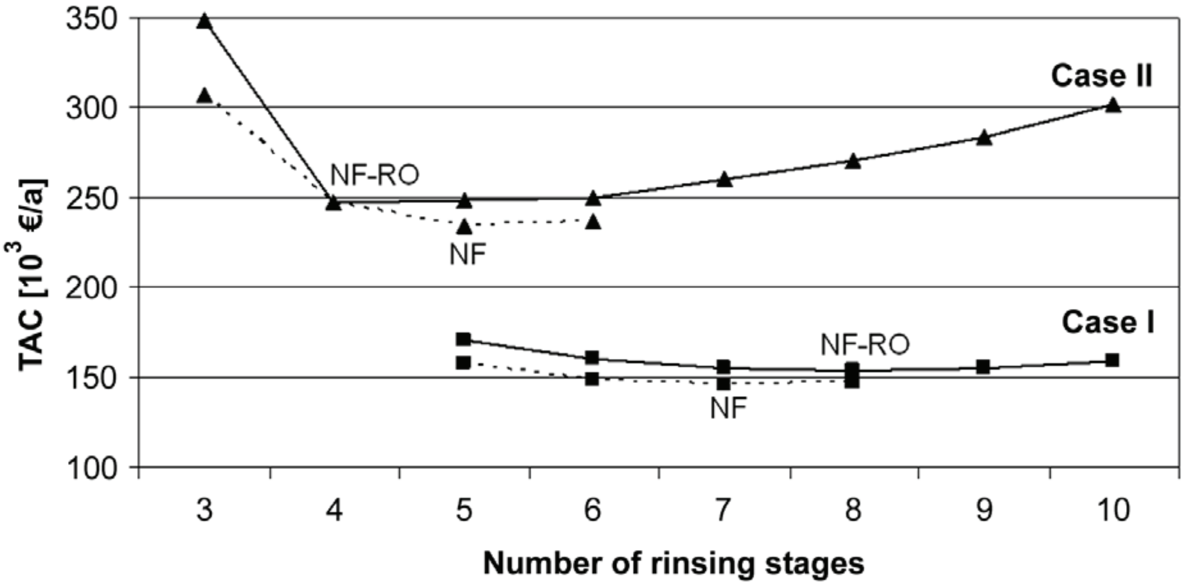

Figure 21: Optimal and suboptimal number of rinsing stages for different β-values: Straight lines indicate β=$10^7$ (equally weighted environmental objective), dashed lines β=$10^5$ (weaker weighted

environmental objective). Triangles: spray rinsing process (Case I), squares: immersion process (Case II). (Erol & Thöming, 2006)

With respect to the invest costs of rinsing stages two cases were distinguished: In case I, the eco-optimum design of the phosphating RRN reaches its minimum at TAC 153,708 €/a (case I, $\beta=10^7$) requiring 8 rinsing stages with both nanofiltration (NF) and reverse osmosis (RO) as regenerators. This optimum design substituting the standard-case has 90 % recovery of nickel in process bath solution. Considering higher periphery-costs as done in case II with the same β-value ($\beta=10^7$) the minimum is reached by 4 rinsing stages at TAC= 246,781 €/a.

For higher β-values ($\beta=10^8$ or $10^9$) the optimum design has the same structure as $\beta=10^7$, but for lower β-values ($\beta=10^5$ to 1) the optimum design tends to have higher number of rinsing stages. For $\beta=10^5$ the optimum design reaches its minimum at TAC=145,490 €/a requiring 7 rinsing stages with only NF as regenerator unit. If the model is obliged to have 8 rinsing stages under certain constraints, than the tendency to produce wastewater is greater than to recover and recycle the rich streams.

The lower the wastewater discharge is aimed, the higher the corresponding costs become. In such cases the system tries to achieve the same key parameter concentration with fewer rinsing stages. This is more costly as it applies an additional regenerator to achieve this target. The consequences are hidden wastes and economic discharges in form of energy consumption. To avoid this drawback the TAC minima can be preferably achieved through applying higher number of rinsing stages than an extra regenerator. The tendency for this is to be seen in Figure 21, to have less regeneration unit (only NF without applying an UO) when the solution is more focused on costs.

The hidden waste in a phosphating-rinsing system relative to a standard case (as in Figure 20: three fold rinsing with Zn-precipitation but without any regeneration) is examined in Figure

22. As water consumption and toxicology like environmental impacts are reduced, the energy consumption accelerated, which also causes depletion of resources. As the energy is to be reduced, then the water consumption is higher and referring to that more wastewater is produced, which means higher toxicology and environmental burdens. This dilemma gets worse with increasing β-values.

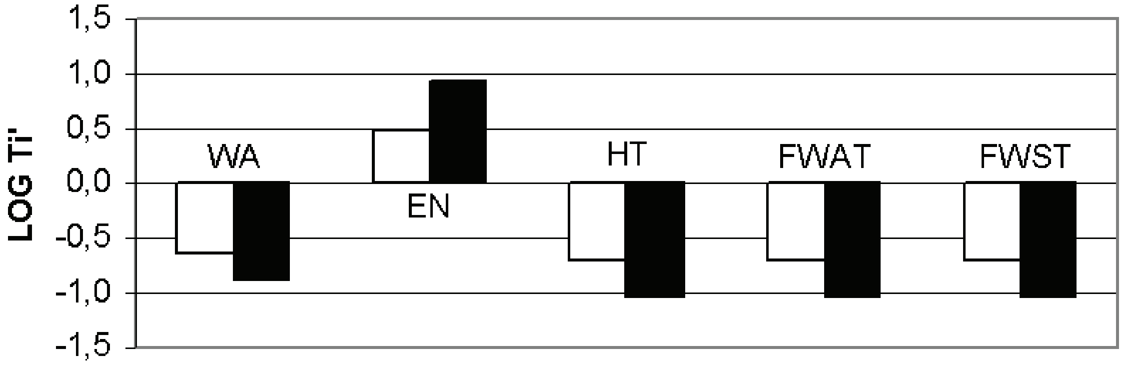

Figure 22: Environmental dilemma of regeneration illustrated by relative environmental impact results (Ti') for two of global optima, case I. WA: water consumption, EN: energy consumption, HT: human toxicity indicator, FWAT: fresh water aquatic toxicity, FWST: fresh water sediment toxicity. White column: weakly weighted ecological aspects ($\beta=10^5$), dark column: equally weighted economic and ecological aspects ($\beta=10^7$). (Erol & Thöming, 2006)

The relative increase scores $T_{i'}$ for each environmental impact category on logarithmic scale in Figure 22 point out the environmental relevance of the system's alternatives. The minimization of the environmental impacts shows results on negative plane of logarithmic scale. Contrary to the preceding circumstance, the worsening in form of energy consumption is to be seen on the positive plane of logarithmic scale since there is an increase in comparison to the standard case. Increasing the β-values from $\beta=10^5$ to $\beta=10^7$, which shifts the alternative solutions from weaker weighted environmental aspects to the equally weighted environmental and economic aspects, approximately a 50 % improvement of toxicity and depletion of resources effects are reached.

The systematic analysis method SAEIS poses the above described dilemma as it figures out the representative (most sensitive) indicator result for the system by an approximation of maximum. Due to the separate consideration of depletion of resources caused by energy consumption in SAEIS, the contrary behavior of this impact category is not disregarded but particularly emphasized and retained to be minimized in the multi objective optimization process.

### 5.3. Concluding Remarks and Outlook

In this work, a sensitivity based quantitative comparison between various environmental impacts (SAEIS) of water based processes is introduced for deriving the most sensitive environmental impact category for the system and integrated into a multi-objective optimization procedure. In this form different objectives are not aggregated into a single objective as it is the case with other methods that aggregate individual preferences. This is particularly relevant in the LCA context, in which it avoids the controversial and debatable aggregation of environmental impacts into a single one in valuation stage. Integration of LCA has two main purposes in this context: one is to quantify and evaluate the environmental performance of a process for choosing sustainable options. Another is to provide a basis for assessing potential improvements in the environmental performance of a system. Therefore mixed-integer non-linear programs (MINLP) are deployed for trading-off the environmental impact and total annualized costs simultaneously.

The applicability of the proposed method has been described and demonstrated in case studies of synthesis of metal finishing line. The eco-optimal design alternatives (RRNs) to the conventional standard case (RN) are investigated.

The proposed synthesis methodology has the potential to signify the “hidden” contribution of energy consumption to environmental burdens, since it is considered separate from water consumption within the impact category depletion of resources. This mostly absorbs the effect of energy consumption because of great amounts consumed in comparison to the quantity of energy resources utilized.

The case studies investigated allow to conclude that the approach can be applied for further investigation of environmental relevance of water based processes. Therefore, it should be tested to enclose SAEIS in a loop, which allows to reduce both total cost and environmental impact. By this means it should be possible to show the side-effects of this minimization of energy consumption within the environmental benign solutions to prevent the possibility of a worsening on the other indicator results. Furthermore such a sequence should generate the Pareto Front including these environmental benign solutions as local optima. In case of a solver which can guarantee the global optima, then this loop can be applied for inspecting the global optimum reached by a solver.

For the risk of higher mathematical complexicity detailed models of regeneration and recycling units could be integrated into the network model instead of assuming constant removal ratio for their efficiency. This will enable to track the chemical and physical changes within these operations throughout the rinsing and recycling sequence and to consider the functional limitations of specific operations.

Flowsheeting systems for process simulation integrated with different programs are often used in process design, process optimization, process integration and process synthesis. SAEIS can be embedded in flowsheeting packages, which as user-friendly expert systems provide modelling aids by knowledge of flowsheeting and models for individual process units. In general there are three approaches for process optimization like sequential modular approach, equation oriented approach and a combination of both (Perkins et al., 1996). Two-stage method combines sequential modular approach and equation oriented approach with main program and subprogram components (Futterer & Munsch, 1990). Main program controlls progress of the calculations and holds unit operation models. There is a need to employ material data from various databases for defining process parameters. Subprograms (routines) are necessary for input and output data and have numeric methods for solving equation systems. In two-stage method since the main idea is the use of complex and simplified models alternately, the complex models are used in sequential modular part and the simplified models are either linearized or non-linear models are solved by iterative solution routines of the equation oriented part. These are arranged in exterior and interior loops (Blass, 1997). SAEIS with its equation oriented approach can be integrated in such an expert system in interior loop, where the solution of reduced problem is aimed with trade-offs. Weighting of trade-offs in the objective function could be implemented in iterative solutions routines of the system.

# APPENDIX - I

## Mathematical Model of RRN for Nickel Plating Case

### Operational equations

For **all rinsing units** $R_r$ operational equations of the type shown in Equation AI-1 were used, where $K_r$ is the rinsing equilibrium constant, $X_r$ is the composition of the lean stream leaving rinsing unit *r*, and $Y_r$ is the composition of the rich stream leaving the same unit *r*.

$$X_r^{out} = K_r \cdot Y_r \qquad \forall r \in R \tag{AI-1}$$

The **separation target** was implemented in form of the rinsing criterion *RC* (Equation AI-2).

$$RC = Y_0 / Y_1 \tag{AI-2}$$

The **performances of the concentrators**, which are explained in the case study section latter, were considered by Equation AI-3.

$$X_c^{out} = K_c \cdot X_c \qquad \forall \text{ c} \in \text{CU *} \tag{AI-3}$$

The total wastewater amount:

$$W_{tot} = \sum_{r \in R} Q_{W,r} + \sum_{c \in CU} (C_{W,c} + D_{W,c}) \tag{AI- 4}$$

The **open-loop** condition is represented by Equation AI-4 where the wastewater and the the water used for bath makeup has to be replaced by fresh water.

$$F = W_{tot} + \sum_{c \in CU} C_{R,c} \tag{AI- 5}$$

**Heuristical Rule** : The amount of concentrate is recycled and substitutes the drag out.

$$D = \sum_{c \in CU} C_{R,c} \qquad \text{(AI- 6)}$$

A set of **rinsing stage and concentrator conditions** was added to avoid overflow of the tanks (Equations AI-7a, AI-7b)

$$Q_r \leq Q_{max}\, y_r \ \ \forall\, r \in R, \qquad y \in \{0,1\}^n \qquad \text{(AI- 7a)}$$

$$Q_c \leq \sum_r y_r \cdot Q_{max} \ \ c = RO, \qquad y \in \{0,1\}^n \qquad \text{(AI- 7b)}$$

**Material balances** were formulated for the carrier liquids for each concentrator unit $CU_c^*$, i.e. electrodialysis (ED) and reverse osmosis (RO) and IX *(*Equation AI-8a, AI-8b), for all rinsing stages $R_r$ (Equation AI-9), for each mixer $M_{i,j}$ *(*Equations AI-9 to AI-11), and for all splitters $S_{i,j}$ (Equations AI-13 to AI-15). The same was done for the **compound material balances** (Equations AI-16 to AI-19b) except for splitters because splitters show identical composition for inlet and outlet streams. Finally, **non-negativity constraints** were applied for all unit operations (UO) on the flowrates and concentrations (Inequalities AI-20a to AI-20d).

**Material balances**

For all concentrator units $CU_c$:

The flow in concentrators split into concentrate and dilute flow:

$$Q_c = C_c + D_c \qquad \forall\, c \in CU \qquad \text{(AI-8a)}$$

As there is no concentrate flow in IX we get:

$$Q_{IX} = D_{IX} \quad \text{and} \quad CIX = 0 \qquad \text{(AI-8b)}$$

For all rinsing stages $R_r$:

$$Q_r^{in} = Q_r^{out} \quad \forall r \in R \tag{AI-9}$$

For all mixers $M_{r,c}$:

$$Q_c = \sum_r Q_{r,c} \quad c \in CU^* \tag{AI-10}$$

For all mixers $M_{c,r}$:

$$Q_r^{in} = \sum_{c \in CU^*} Q_{c,r} + Q_{r-1,r} \quad \forall r \in R, \quad r \neq 1 \tag{AI-11}$$

$$Q_r = \sum_{c \in CU^*} Q_{c,r} + F \qquad r = 1 \tag{AI-12}$$

For all splitters $S_{c,r}$:

$$Q_c^{out} = \sum_r Q_{c,r} \quad \forall c \in CU^* \tag{AI-13}$$

For all splitters $S_{r,c}$:

$$Q_r^{out} = \sum_{c \in CU^*} Q_{r,c} + Q_{r,r+1} + Q_{w,r} \qquad \forall r \in R, \qquad r \neq 1,8 \tag{AI-14a}$$

$$Q_r^{out} = \sum_{c \in CU^*} Q_{r,c} + Q_{w,r} \qquad r = 8 \tag{AI-14b}$$

$$Q_r^{out} = \sum_{c \in CU^*} Q_{r,c} + Q_{r,r+1} \qquad r = 1 \tag{AI-14c}$$

For all splitters $S_{C,c}$ in the concentrators concentrate stream is:

$$C_c = C_{W,c} + C_{R,c} \qquad c \in CU \tag{AI-15}$$

### Compound material balances

For all concentrator units:

$$Q_c \cdot X_c = C_c \cdot Y_c + D_c \cdot X_c^{out} \qquad c \in CU^* \tag{AI-16}$$

For all rinsing stages $R_r$:

$$D \ \cdot Y_{r+1} + Q_r \cdot X_r^{in} = D_r \cdot Y_r + Q_r \cdot X_r^{out} \qquad \forall r \in R \ \text{ with } Y_9 = Y_0 \tag{AI-17}$$

For all mixers $M_{r,c}$ before the concentrators:

$$Q_c \cdot X_c = \sum_r Q_{r,c} \cdot X_r \qquad \forall\ c \in CU^* \tag{AI-18}$$

For all mixers $M_{c,r}$ before the rinsing stages:

$$Q_r \cdot X_r = \sum_{c \in CU^*} Q_{c,r} \cdot X_c + Q_{r-1,r} \cdot X_{r-1}^{out} \qquad \forall \mathrm{r}\ \in \mathrm{R},\ \mathrm{r} \neq 1 \tag{AI-19a}$$

$$Q_r \cdot X_r = \sum_{c \in CU^*} Q_{c,r} \cdot X_c \qquad r = 1 \tag{AI-19b}$$

Nonnegativity

$$\mathrm{X_i} \geq 0 \ \ \forall\ \mathrm{i} \in \mathrm{UO} \tag{AI-20a}$$

$$\mathrm{Y_i} \geq 0 \ \ \forall\ \mathrm{i} \in \mathrm{UO} \tag{AI-20b}$$

$$\mathrm{Q_i} \geq 0 \ \ \forall\ \mathrm{i} \in \mathrm{UO} \tag{AI-20c}$$

$$\mathrm{C_c} \geq 0 \ \ \forall\ \mathrm{c} \in \mathrm{CU} \tag{AI-20d}$$

The **feasibility region** of the optimization problem is described by both Equations AI-1 to AI-19 and Inequalities AI-20a to AI-20d.

## Energy Consumption

The total energy consumption contains the energy consumption of the concentrator units (Equation AI-21)

$$EN_j = Q_{D,j} \cdot spezE_j * CF \qquad \forall j \in \text{CU} \tag{AI-21}$$

and the used energy for pumping the freshwater stream (Equations AI-22a, AI-22b). The needed energy $EN_{p,F}$ is divided by the pumping efficiency $\eta$ to get the amount of energy to be provided for pumping.

$$EN_{p,F} = f \cdot spezW \cdot F \cdot CF \tag{AI-22a}$$

$$EN_p = \frac{EN_{p,F}}{\eta} \tag{AI-22b}$$

The sum of all this energy consumptions will lead to the total energy consumption $EN_{tot}$ (Equation AI-23).

$$EN_{tot} = EN_p + \sum_{j \in CU} EN_j \tag{AI-23}$$

## Total Annual Costs

The total annualized cost (*TAC*) depends on the operational cost $OC_i$ of unit operation $UO_i$, which is annualized by the conversion factor CF = 8000 h $a^{-1}$ (Equation AI-25). The variable $CP_i$ is the cost parameter, and $Q_i$ is the flowrate of that stream *i* to which $CP_i$ refers. PC is the pumping cost for fresh water stream. (All other pumping costs are already included in cost function of regenerators).

$$TAC = \sum_{i \in UO} \left( OC_i + \frac{CC_i}{AD} \right) + \sum_{s \in S_0} CC_s + PC \tag{AI-24}$$

$$OC_i = CP_i \cdot Q_i \cdot CF \quad \forall \text{ i} \in \text{UO}, \tag{AI-25}$$

The *TAC* also depends on the capital costs $CC_i$ that are annualized by the annual depreciation factor AD = 5 a (Equations AI-26a to AI-26c). The variables $CC_c$ are calculated using the exponent $\alpha_c$ and two reference values, $CP_{i,0}$ and $Q_{i,0}$, for the costs and the flowrate respectively. All these data are determined empirically (Wright & Woods, 1993; Wright & Woods, 1995). TAC is calculated in $\$a^{-1}$ and results are given in € $a^{-1}$ for an estimated exchange-rate of 1:1(1$=1€).

Capital cost for rinsing stages:

$$CC_R = CP_{R,0} \cdot \sum_{r \in R} y_r \qquad \text{y} \in \{0,1\}^{\text{n}} \tag{AI-26a}$$

Capital cost for all concentrators:

$$CC_c = n \cdot CP_{c,0} \cdot \left( \frac{Q_c \cdot X_c}{(n-1) \cdot Q_{c,0}} \frac{t_s}{CAP} \right)^{\alpha_c} \qquad \text{c = IX} \tag{AI-26b}$$

where n is the number of IX units.

$$CC_c = CP_{c,0} \cdot \left( \frac{Q_c}{Q_{c,0}} \right)^{\alpha_c} \qquad \forall \text{ c} \in \text{CU} \tag{AI-26c}$$

Furthermore TAC depends on the costs for used chemicals $S_0$ that is Ni and $H_20$, which are annualized by the convertion factor CF=8000 $ha^{-1}$ (Eq.27).The variable $MIND_s$ (E q.28a,b) is the annual amount in kg needed from substance s. $KC_s$ is the cost for kg substance.

$$CC_s = KC_s \cdot MIND_s \qquad \forall \text{ s} \in S_0=\{\text{Ni}, H_20\} \tag{AI-27}$$

**Mass Index for the substances Ni and $H_2O$:**

$$MIND_{Ni} = \sum_r Q_{W,r} \cdot X_r^{out} + \sum_{c \in CU} (C_{W,c} \cdot Y_c + D_{W,c} \cdot X_c^{out}) \cdot CF \qquad \text{(AI-28a)}$$

$$MIND_{H_2O} = F \cdot CF \qquad \text{(AI-28b)}$$

Mass index for energy resources which are soft coal (SC), hard coal (HC), natural gas (NG) and crude oil (CO):

$$MIND_s = \frac{EN_{tot} \cdot Frac_s}{f \cdot h_s \cdot WG_s} \qquad \text{(AI-29)}$$

Where $EN_{tot}$ is the total amount of energy used in kWh, $Frac_s$ is the fraction of energy from the energy mixture of Germany in 2002, that is provided by energy resource $s$, $h_s$ is the heating value $MJ/m^3$ of $s$ per kg,$WG_s$ is the efficiency of energy production using $s$ and f is a conversion factor which converts MJ to kWh.

Environmental Impact Indicator value for each indicator category related with considered substance:

$$IND_{i,s} = CF_{i,s} \cdot MIND_s \qquad i \in IC, \qquad s \in S \qquad \text{(AI-30)}$$

IC is the set of considered impact categories:

IC = human toxicity, fresh water aquatic toxicity, fresh water sediment, depletion of abiotic resources.

The Ti value for each impact category is:

$$T_i = \sum_s IND_{i,s} \qquad i \in IC \qquad \text{(AI-31)}$$

The relative value of environmental impact indicator for each indicator category is:

$$T_i' = \frac{T_i}{T_{\mathrm{Re}\,f,i}} \qquad i \in IC \tag{AI-32}$$

The maximal relative value of environmental impact indicator out of all indicator category is:

$$T_{\max}' = \max_{i \in IC} \tilde{T}_i' \tag{AI-33}$$

Multi-objective function:

$$\min ZF = TAC + \beta \cdot \tilde{T}_{\max}' \tag{AI-34}$$

The **minimization of the objective function ZF** that is **subject to the constraints** which form the feasibility region is referred to as a mixed-integer nonlinear program (MINLP). This is due to (a) the non-linearity of Equations AI-16 to AI-19b and AI-26a, AI-26b and (b) the binaries in the Equations AI-7a, AI-7b and AI-26a. The MINLP is recognized as the most sophisticated type of optimization program (Edgar et al., 2001). It is usually difficult to solve especially if the variables are not properly initialized (Grossmann & Kravanja, 1995). The solution of the MINLP, modeled in GAMS, version 21.2 (GAMS, 2000), gives the unit interconnections, the flow rates and concentration of each stream in the hyperstructure and the number of rinsing stages.

## Mathematical Model for Open-loop Standard Case (RN)

Analog to the open-loop RRN model here the open-loop standard RN model will be formulized.

### Operational equations

For **all rinsing units** $R_r$ operational equations of the type shown in Equation AI-35 were used, where $K_r$ is the rinsing equilibrium constant, $X_r$ is the composition of the lean stream leaving rinsing unit $r$, and $Y_r$ is the composition of the rich stream leaving the same unit $r$.

$$X^{out}{}_r = K_r\, Y_r \quad \forall r \in R \tag{AI-35}$$

The **separation target** was implemented in form of the rinsing criterion $RC$.

$$RC = Y_0 \,/\, Y_1 \tag{AI-36}$$

A set of **rinsing stage conditions** was added to avoid overflow of the tanks

$$\mathrm{Q_r \leq Q_{max}\ \forall\ r \in R} \tag{AI-37}$$

**Material balances** were formulated for all rinsing stages $R_r$ (Equation AI-38).The same was done for the **compound material balances** (Equations AI-39). Finally, **non-negativity constraints** were applied for all unit operations (UO) on the flowrates and concentrations (Inequalities AI-40a to AI-40c).

### Material balances

For all rinsing stages $R_r$:

$$Q_r^{in} = Q_r^{out} = F \tag{AI-38}$$

**Compound material balances**

For all rinsing stages Rr:

$$F \cdot X_{r-1}^{out} + D \cdot Y_{r+1} = F \cdot X_{r}^{out} + D \cdot Y_{r} \qquad \forall r \in R \qquad (\text{AI-39})$$

with

$$X_{r-1}^{out} = 0 \ (Freshwater\,Concentration)$$

$$Y_4 = Y_0 \ (initial\,drag\,out\,Concentration)$$

Nonnegativity

$$X_i \geq 0 \ \ \forall \ i \in UO \qquad (\text{AI-40a})$$

$$Y_i \geq 0 \ \ \forall \ i \in UO \qquad (\text{AI-40b})$$

$$Qi \geq 0 \ \ \forall \ i \in UO \qquad (\text{AI-40c})$$

The **feasibility region** of the optimization problem is described by both Equations AI-35 to AI-39 and Inequalities AI-40a to AI-40c.

**Energy Consumption**

Due to the fact that there is no concentrator unit in the open-loop standard case the energy consumption contains only of the contribution of the energy consumption for pumping the freshwater.

The needed energy $EN_{p,F}$ is divided by the pumping efficiency $\eta$ to get the amount of energy to be provided for pumping.

$$EN_{p,F} = f \cdot spezW \cdot F \cdot CF \tag{AI-41a}$$

$$EN_{p} = \tfrac{EN_{p,F}}{\eta} \tag{AI-41b}$$

The total energy consumption $EN_{tot}$ is equal to the energy consumption for pumping:

$$EN_{tot} = EN_{p} \tag{AI-42}$$

**Total Anual Costs**

The total annualized cost (*TAC*) depends on the operational cost $OC_i$ of unit operation $UO_i$, which is annualized by the conversion factor CF = 8000 h $a^{-1}$ (Equation AI-44). The variable $CP_i$ is the cost parameter, and $Q_i$ is the flowrate of that stream *i* to which $CP_i$ refers. . PC is the cost for pumping the fresh water stream. (All other pumping costs are already included in other terms).

$$TAC = \sum_{i \in UO} \left( OC_i + \frac{CC_i}{AD} \right) + \sum_{s \in S_0} CC_s + PC \tag{AI-43}$$

$$OC_i = CP_i \cdot Q_i \cdot CF \quad \forall \text{ i} \in \text{UO}, \tag{AI-44}$$

The *TAC* also depends on the capital costs $CC_i$ that are annualized by the annual depreciation factor AD = 5 a (Equation AI-45). The variables $CC_c$ are calculated using the exponent $\alpha_c$ and two reference values, $CP_{i,0}$ and $Q_{i,0}$, for the costs and the flowrate respectively. All these data are determined empirically (Wright & Woods, 1993; Wright & Woods, 1995).

$$CC_R = CP_{R,0} \cdot \sum_{r \in R} y_r \qquad \text{y} \in \{0,1\}^{n} \tag{AI-45}$$

Furthermore TAC depends on the costs for used chemicals $S_0$ that is Ni and $H_20$, which are annualized by the convertion factor CF=8000 $ha^{-1}$ (Eq. AI-46).The variable $MIND_s$ (Eq. AI-

47a, AI-47b) is the annual amount in kg needed from substance s. $KC_s$ is the cost for kg substance.

$$CC_s = KC_s \cdot MIND_s \qquad \forall\ s \in S_0 \tag{AI-46}$$

$$MIND_{Ni} = \sum_r Q_{w,r} \cdot X_r^{out} + \sum_{c \in CU} (C_{w,c} \cdot Y_c + D_{w,c} \cdot X_c^{out}) \cdot CF \tag{AI-47a}$$

$$MIND_{H_2O} = F \cdot CF \tag{AI-47b}$$

Environmental Impact Indicator value for each indicator category related with considered substance:

$$IND_{i,s} = CF_{i,s} \cdot MIND_s \qquad i \in IC,\ s \in S \tag{AI-48}$$

The Ti value for each impact category: This value will be taken as the reference value $T_{Ref,i}$ in the open-loop RRN case.

$$T_i = \sum_s IND_{i,s} \qquad i \in IC \tag{AI-49}$$

## Nomenclature

| | | |
|---|---|---|
| AD | Annual depreciation | a |
| C | Concentrator unit index | - |
| $C_c$ | Concentrated recycle stream of unit c | g $h^{-1}$ |
| CAP | Capacity of IX resin | g $m^{-3}$ |
| $CC_i$ | Capital costs of unit i | € $a^{-1}$ |
| CF | Conversion factor | h $a^{-1}$ |
| $CF_{i,s}$ | Characterization Factor for impact category indicator i for substance s | |
| $CP_i$ | Cost parameter of unit i | € $h^{-1}$ |
| $CP_{i,0}$ | Reference cost parameter of unit i | € $a^{-1}$ |
| $C_{R,c}$ | Concentrate recycling stream for c | kg $h^{-1}$ |
| $C_s$ | Cost per kg of Substance (Chemicals) | kg $h^{-1}$ |
| $C_{W,c}$ | Concentrate wastewater stream for c | kg $h^{-1}$ |
| CU | Concentrator unit = {RO,ED} | - |
| CU* | Concentrators = {RO,ED,IX} | - |
| $D_c$ | Dilute stream for c | kg $h^{-1}$ |
| $D_0$ | Drag-out entering the initial rinse | kg $h^{-1}$ |
| $D_r$ | Drag-out off the rinse r | kg $h^{-1}$ |
| $D_{W,c}$ | Dilute wastewater stream for c | kg $h^{-1}$ |
| ED | Electrodialysis | - |
| F | Freshwater flow rate | kg $h^{-1}$ |
| i | Unit operation index | - |
| IC | Set of impact categories | - |
| $IND_{i,s}$ | Indicator value for impact category i and substance s | - |

| | | |
|---|---|---|
| IX | Ion exchange | - |
| $K_i$ | Equilibrium constant of unit i | - |
| $KC_s$ | Cost for kg substance (chemical) | € kg$^{-1}$ |
| L | Flowrate of IX regeneration liquid | kg h$^{-1}$ |
| $M_{i,j}$ | Mixer after unit i ahead of unit j | - |
| $MIND_s$ | Mass index for substance s | kg h$^{-1}$ |
| $OC_i$ | Operation costs of unit i | € a$^{-1}$ |
| $Q_i$ | Flowrate into unit i | kg h$^{-1}$ |
| $Q_{i,0}$ | Reference flowrate | kg h$^{-1}$ |
| $Q_{i,j}$ | Flowrate from unit i into unit j | kg h$^{-1}$ |
| $Q^{out}_c$ | Flowrate of reused part of dilute stream | kg h$^{-1}$ |
| $Q_{W,r}$ | Wastewater stream for rinsing stages | kg h$^{-1}$ |
| $r$ | Rinsing stage index | - |
| $R_r$ | Rinsing stage r | - |
| $RC$ | Rinsing criterion | kg h$^{-1}$ |
| $RO$ | Reverse osmosis | - |
| $S$ | Substances = {Ni,$H_20$, SC, HC, NG, CO} | - |
| $S_0$ | Substances ={Ni, $H_20$} | - |
| $S_1$ | Substances ={ SC, HC, NG, CO } | - |
| $s$ | Splitter index | - |
| $S_{i,j}$ | Splitter after unit i ahead of unit j | - |
| $TAC$ | Total annualized costs | € a$^{-1}$ |
| $T_i$ | Environmental impact category indicator value | - |
| $T_i^{'}$ | Relative value of $T_i$ | - |
| $T_{Ref,i}$ | Reference value for $T_i$ *(for a 3 stage rinsing case)* | - |
| $T_i^{'}max$ | Max $T_i$ value of all environmental impact indicators | - |

| | | |
|---|---|---|
| $UO$ | Unit operations | - |
| $W$ | Water makeup | kg $h^{-1}$ |
| $W_{tot}$ | Total wastewater flow rate | kg $h^{-1}$ |
| $X_i$ | Key-component composition in the lean stream entering unit i | g $kg^{-1}$ |
| $X^{out}_i$ | Key-component composition in the lean stream leaving unit i | g $kg^{-1}$ |
| $Y_i$ | Key-component composition in the rich stream leaving unit i | g $kg^{-1}$ |
| $Y$ | Solution vector y of integer variables | - |
| $ZF$ | Objective Function | - |
| $\alpha$ | Exponent of cost function | - |
| $\beta$ | Weighting factor for environmental impacts versus annual costs | - |
| $EN_p$ | Energy consumption of pumps | Wh/a |
| $EN_{p,F}$ | Energy consumption of pumps for the freshwater stream | Wh/a |
| $EN_j$ | Energy consumption of concentrator unit j | Wh/a |
| $EN_{tot}$ | Totatl energy consumption | Wh/a |
| PC | Pumping cost | €/a |
| spezW | Specific work for a **Kreiskolbenpumpe** | Wh/kg |
| $spezE_j$ | Specific energy consumption of concentrators | Wh/kg Permeat |
| $\eta_p$ | Pump efficiency of pumps | - |
| $\eta_{elek}$ | Electric efficiency of pumps | - |
| $\eta$ | Total efficiency of pumps | - |
| $FRAC_s$ | Fraction of s in the energy mixture of Germany in 2002 | - |
| $h_s$ | Heating value per kg energy resource s | MJ/m3 |
| $WG_s$ | Effiency of energy production using energy resource s | - |

# APPENDIX - II

## Mathematical Model of RRN for Phosphating Case

To easily handle the complex model, a classification into rinsing, concentrators, effluent treatment, mass, energy, eco and cost modules is carried out. Each physical content is described by mass, compound and energy balances.

The modules that enlighten the ECO-optimization model are as follows:

### Basic modules

The rinsing module was further divided into three submodules namely; Mixers prior to rinsing, rinsing stages, splitters after rinsing. The material balances of the *mixers* describe the reused water inflow from the concentrators $Q_S^{j,i}$, the back stream from other rinsing stages $Q_R^{i-1,i}$ and the fresh water supply $F_R$ :

$$\sum_{j\in J} Q_S^{J,1} + \mathrm{F_R} = \mathrm{Q}^1 \tag{AII-1}$$

$$\sum_{j\in J} Q_S^{j,i} + \mathrm{Q}_R^{\mathrm{i-1,i}} = \mathrm{Q}^{\mathrm{I}} \,, \mathrm{i} > 1 \tag{AII-2}$$

The compound balance equations provide the concentration (X) of the trace elements (t) in the mixers:

$$\sum_{j\in J} X_D^{j,t} \, \mathrm{Q_S^{j,1}} + 0 \,\mathrm{x}\, \mathrm{F_R} = \mathrm{X_{in}^{1,t}} \, \mathrm{Q}^1 \quad \forall\, \mathrm{t} \tag{AII-3}$$

$$\sum_{j\in J} X_D^{j,t} \, \mathrm{Q_S^{j,i}} + \mathrm{X}_{out}^{\mathrm{i-1,t}} \, \mathrm{Q_R^{i-1,i}} = \mathrm{X_{in}^{i,t}} \, \mathrm{Q^i} \quad \forall\, \mathrm{t, i} > 1 \tag{AII-4}$$

The pre-conditions in the rinsing module are the rinsing criteria (R) and the flow rate limitations $Q_{max}$ given by:

$$Y_0^t = \mathrm{RY}^{1,t} \quad \forall\, t \tag{AII-5}$$

Where, the rinsing criterion (R) defines the separation target as proportion of drag-out concentrations in the initial rinsing to the final one.

$$Q^i \text{ - Qmax } \mathrm{z}^{\mathrm{i}} \;\leq 0 \;\; \forall \;\; \mathrm{i} \tag{AII-6}$$

An additional constraint is deployed to prevent a stage jump. For example, if there are 6 stages, only R1 up to R6 have to exist and not, that is R1 up to R5 and R7 in addition. This constraint implies that, if a rinsing stage exists, all others with smaller numbers also have to exist.

$$Z^i \geq \mathrm{Z}^{\mathrm{i}} + 1 \quad \forall\, \mathrm{i} \tag{AII-7}$$

The splitter module describes the mass and compound balances after the rinsing stages which divides the stream into three streams: one to the concentrators $\mathrm{QSP}^{i,j}$, the second one to the wastewater outflow $Q_W{}^i$ and the third one is the back stream to the next rinsing stage $Q_R{}^{i,i+1}$.

$$Q^i = \sum_{\mathrm{j}\in\mathrm{J}} Q_{SP}^{i,i+1} + \mathrm{Q}_R^{\mathrm{i,i+1}} + \mathrm{Q}_{\mathrm{W}}^{\mathrm{i}} \quad \forall\, \mathrm{i} \tag{AII-8}$$

$$X_{in}^{i,t}\ \mathrm{Q}^{\mathrm{i}} + \mathrm{Y}^{\mathrm{i+1,t}}\ \mathrm{D} = \mathrm{X}_{\mathrm{out}}^{\mathrm{i,t}}\ \mathrm{Q}^{\mathrm{i}} + \mathrm{Y}^{\mathrm{i,\,t}}\ \mathrm{D} \;\; \forall \mathrm{t}, \mathrm{i} < \mathrm{i}_{\mathrm{e}} \tag{AII-9}$$

$$X_{in}^{i_e,t}\ \mathrm{Q}^{\mathrm{i_e}} + \mathrm{Y}_0^{\mathrm{t}}\ \mathrm{D} = \mathrm{X}_{out}^{\mathrm{i_e},t}\ \mathrm{Q}^{\mathrm{i_e}} + \mathrm{Y}^{\mathrm{i_e,t}}\ \ \mathrm{D} \;\; \forall\, \mathrm{t} \tag{AII-10}$$

From the superstructure it is observed that there will be no direct flow $Q_{SP}{}^{i,RO}$ from these splitters to the RO unit, therefore:

$$Q_{SP}^{i,RO} = 0 \quad \forall\, \mathrm{i} \tag{AII-11}$$

The matching of rinsing stream $X_{out}{}^{i,t}$ and drag out stream $Y^{i,t}$ is done by fixing.

$$X_{out}^{i,t} = \mathrm{Y}^{i,t} \quad \forall\, i, t \tag{AII-12}$$

An additional constraint as heuristic rule has been introduced, in order to have wastewater discharge $Q_W^i$ only at the last rinsing stage.

$$Q_W^i \leq 10^6 \ (z^i - z^{i+1}) \ \ \forall \ i \tag{AII-13}$$

The factor $(z^i - z^{i+1})$ will be 1 only for the last rinsing stage and 0 otherwise. Therefore the above given inequality limits the wastewater flow of all but the last rinsing stage to 0.

**Concentrator Module:** The concentrator module in general describes the special properties of the specific concentrator units. Following mass and compound balance and energy consumption equations provide the stream quantities (such as flow rates of concentrator inlet stream$Q_J^j$, concentrate stream$Q_C^j$, dilute stream$Q_D^j$ and concentrations (X) of each stream) for both concentrators:

$$Q_J^j = \mathrm{Q}_C^j + \mathrm{Q}_D^j \quad \forall\, j \tag{AII-14}$$

$$\mathrm{X}_D^{j,t}\, \mathrm{Q}_D^j = \mathrm{SplitF}^{j,t} \ \ \mathrm{X}_J^{j,t} \ \mathrm{Q}_J^j \quad \forall\, j, t \tag{AII-15}$$

By means of *nanofiltration sub-module* the NF unit is to exist in the model that is at least 1 l/h will pass the unit:

$$\mathrm{Q}_D^{NF} \geq 1 \tag{AII-16}$$

Without this constraint the model sometimes finds solutions without any concentrators (as a local optimum) like in standard case. Influent to NF unit $Q_J^{NF}$ originates from the splitter after the rinsing module:

$$\mathrm{Q}_J^{NF} = \sum_{i \in I} \mathrm{Q}_{SP}^{i,NF} \tag{AII-17}$$

The NF unit separate the influent into dilute and concentrate stream. The dilute stream flow rate is calculated by:

$$Q_D^{NF} = \mathrm{DC\_Ratio}^{\mathrm{NF}} \quad \mathrm{Q}_{\mathrm{C}}^{\mathrm{NF}} \tag{AII-18}$$

The dilute stream is split into three sub-streams, namely the stream to RO unit $Q_{CC}^{NF,RO}$, the stream back to rinsing $Q_S^{NF,i}$ and the wastewater stream $Q_{WD}^{NF}$. This is provided by the relation:

$$Q_{\mathrm{D}}^{\mathrm{NF}} = \mathrm{Q}_{\mathrm{CC}}^{\mathrm{NF,\,RO}} + \sum_{\mathrm{i}\in\mathrm{I}} \mathrm{Q}_{\mathrm{S}}^{\mathrm{NF,i}} + \mathrm{Q}_{\mathrm{WD}}^{\mathrm{NF}} \tag{AII-19}$$

On the other hand, the concentrate stream is divided into two sub-streams i.e.: recycling stream back into bath QRecyclNF and wastewater discharge $Q_{WC}^{NF:}$

$$Q_C^{NF} = \mathrm{Q}_{\mathrm{Recycl}}^{\mathrm{NF}} + \mathrm{Q}_{\mathrm{WC}}^{\mathrm{NF}} \tag{AII-20}$$

As a second heuristic rule, a constraint to prevent unphysical solutions (negative fresh water inflow into the bath unit, cf. equation (AII-31)) is introduced, limits the bath recycling stream to the amount of drag out stream (D).

$$Q_{\mathrm{Re}\,cycl}^{NF} \leq \mathrm{D} \tag{AII-21}$$

Compound balances at the inlet and outlet of NF unit are as follows:

$$X_J^{NF,t} \quad \mathrm{Q}_{\mathrm{J}}^{\mathrm{NF}} = \sum_{\mathrm{i}\in\mathrm{I}} \mathrm{X}_{\mathrm{out}}^{\mathrm{i,t}} \quad \mathrm{Q}_{\mathrm{SP}}^{\mathrm{i,NF}} \qquad \forall\, \mathrm{t} \tag{AII-22}$$

and

$$X_J^{NF} \, \mathrm{Q}_{\mathrm{J}}^{\mathrm{NF}} = \mathrm{X}_{\mathrm{C}}^{\mathrm{NF,t}} \quad \mathrm{Q}_{\mathrm{C}}^{\mathrm{NF}} + \mathrm{X}_{\mathrm{D}}^{\mathrm{NF,\,t}} \quad \mathrm{Q}_{\mathrm{D}}^{\mathrm{NF}} \qquad \forall\, \mathrm{t} \tag{AII-23}$$

The **reverse osmosis sub-module** describes the process principle of the RO unit. The inflow is calculated by the sum of rinsing splitter inflow (in our model set to 0, cf. equation (AII-11) and the cross flow from the NF unit.

$$Q_J^{RO} = \sum_{i \in I} Q_{SP}^{i,RO} + Q_{CC}^{NF,RO} \qquad \text{(AII-24)}$$

The amount of the dilute stream is calculated similar to NF unit's:

$$Q_D^{RO} = DC\_Ratio^{RO} \; Q_C^{RO} \qquad \text{(AII-25)}$$

The dilute stream of RO unit is split into the backflow into rinsing and the wastewater stream:

$$Q_D^{RO} = \sum_{i \in I} Q_S^{RO,i} + Q_{WD}^{RO} \qquad \text{(AII-26)}$$

The concentrate stream is completely discharged as wastewater in order to separate the trace elements out of the system that are not used for bath make up.

$$Q_C^{RO} = Q_{WC}^{RO} \qquad \text{(AII-27)}$$

The flow rate through the RO unit is limited by

$$Q_J^{RO} - 5Q_{max} \; Z^{RO} \leq 0 \qquad \text{(AII-28)}$$

The compound balances of RO unit are written as follows:

$$X_J^{RO,t} \; Q_J^{RO} = \sum_{i \in I} X_{out}^{i,RO} \; Q_{SP}^{i,RO} + X_D^{NF,t} \; Q_{CC}^{NF,RO} \quad \forall \, t \qquad \text{(AII-29)}$$

and

$$X_J^{RO,t} \; Q_J^{RO} = X_C^{RO,t} \; Q_C^{RO} + X_D^{RO,t} \; Q_D^{RO} \quad \forall \, t \qquad \text{(AII-30)}$$

The bath module only consists of mass balance

$$F_{Bath} + \mathrm{Q}_{\mathrm{Recycl}}^{\mathrm{NF}} = \mathrm{D} \qquad \text{(AII-31)}$$

The compound balance is used only implicit in the Ni consumption calculation. An explicit calculation is not necessary, because the mass of Ni in the recycling stream always has to be less or equal than the total amount of mass introduced into the system by the drag-out stream and the bath concentration.

The RRN mass balance is given by

$$F_R = \sum_{\mathrm{i \in I}} \mathrm{Q}_{\mathrm{W}}^{\mathrm{i}} + \sum_{\mathrm{j \in J}} \mathrm{Q}_{\mathrm{WC}}^{\mathrm{j}} + \sum_{\mathrm{j \in J}} \mathrm{Q}_{\mathrm{WD}}^{\mathrm{j}} + \mathrm{Q}_{\mathrm{Recycl}}^{\mathrm{NF}} \qquad \text{(AII-32)}$$

(Remark, the bath is not part of the RRN) The total wastewater amount is given by

$$Q_{Wtot} = \sum_{\mathrm{i \in I}} \mathrm{Q}_{\mathrm{W}}^{\mathrm{i}} + \sum_{\mathrm{j \in J}} \mathrm{Q}_{\mathrm{WC}}^{\mathrm{j}} + \sum_{\mathrm{j \in J}} \mathrm{Q}_{\mathrm{WD}}^{\mathrm{j}} \qquad \text{(AII-33)}$$

**Effluent treatment module (Zn-Precipitation):** The whole wastewater amount is lead into the zinc precipitation.

$$Q_{\mathrm{W,in}} = \mathrm{Q}_{\mathrm{Wtot}} \qquad \text{(AII-34)}$$

The rest wastewater which can not be bound in form of metal salts in sludge is to be discharged as wastewater.

$$Q_{\mathrm{W.out}} = \mathrm{SpF}_{\mathrm{W_W}} \ \mathrm{Q}_{\mathrm{W,in}} \qquad \text{(AII-35)}$$

The amount of water bounded in the sludge is the difference between inlet and outlet flow:

$$Q_{SL} = \mathrm{Q}_{\mathrm{W,in}} - \mathrm{Q}_{\mathrm{W,out}} \tag{AII-36}$$

The product of the water amount and the concentration provides the mass of Zn that is to precipitate:

$$X^{Zn}_{W,in}\ \mathrm{Q}_{\mathrm{W.in}} = \sum_{\mathrm{i}\in \mathrm{I}} \mathrm{Q}^{\mathrm{i}}_{\mathrm{W}}\ \mathrm{X}^{\mathrm{i,Zn}}_{\mathrm{out}} + \sum_{\mathrm{j}\in \mathrm{J}} \mathrm{Q}^{\mathrm{j}}_{\mathrm{WC}}\ \mathrm{X}^{\mathrm{j,Zn}}_{\mathrm{C}} + \sum_{\mathrm{j}\in \mathrm{J}} \mathrm{Q}^{\mathrm{j}}_{\mathrm{WD}}\ \mathrm{X}^{\mathrm{j,ZN}}_{\mathrm{D}} \tag{AII-37}$$

The precipitation chemical consumption is calculated related with the mole amount of the metal ions.

$$X^{Zn}_{M} = \frac{\mathrm{X}^{\mathrm{Zn}}_{\mathrm{W,in}}\ \mathrm{Q}_{\mathrm{W,in}} - \mathrm{X}^{\mathrm{Zn}}_{\mathrm{W,out}}\ \mathrm{Q}_{\mathrm{W,out}}}{\mathrm{Mwt}^{\mathrm{Zn}}} \tag{AII-38}$$

**Energy module:** Pumping energy for freshwater inflow $\mathrm{E_F}$ is calculated over a year by attaining the specific work (spezW) for centrifugal piston pump in kJ/kg, flow rate of the streams in kg/h with a conversion factor of 0.28 from kJ to Wh and a conversion factor of 8000 h/a as a mean value of working hours in a year:

$$EF = 0.28 \cdot spezW\ (\mathrm{F_R} + \mathrm{F_{Bath}})\ \mathrm{x}\ 8000 \tag{AII-39}$$

Absolute power requirement for pumping is determined by considering the efficiencies of the pump $(\eta m \cong 90\,\%)$ and motor $(\eta m \cong 70\,\%)$:

$$Ep = \frac{\mathrm{Ef}}{\eta_{\mathrm{p}}\eta_{m}} \tag{AII-40}$$

Energy consumption of concentrators ( $\mathrm{E_j}$ ) is estimated by the specific work (spez$\mathrm{E_j}$) needed per dilute stream flow of each concentrator regarding the assumptions in (Perry & Green, 1997).

$$E^J = \mathrm{Q_D^J}\ \mathrm{spez\ E^J}\ \mathrm{x}\ 8000 \quad \forall\ \mathrm{j} \tag{AII-41}$$

The total amount of energy utilization is ascertained by the sum of pumping and concentrator units' energy consumption:

$$E_{tot} = \mathrm{Ep} + \sum_{\mathrm{j} \in \mathrm{J}} E^J \tag{AII-42}$$

**Cost module**

Mathematical expression for total annualized cost function consists of operational costs (OC) and capital costs (CC) for each unit in the RRN structure. The cost projection assumptions for operational and investment costs are taken from (Wright & Woods, 1995), (Wright & Woods, 1993) and specific regenerator properties from (Perry & Green, 1997).

$$TAC = \frac{\mathrm{OC} + \mathrm{CC^{NF}} + \mathrm{CC^{RO}} + \mathrm{CC_R} + \mathrm{CC_{ZnP}}}{a} \tag{AII-43}$$

The operational costs (OC) depend on the flow rate per unit, the number of used units, the amount of trace elements and energy used, where the cost of the energy for the concentrators are already integrated into the costs per flow rate. These costs are annualized by the conversion factor 8000 h/a. Therefore we get

$$\begin{aligned} OC = &\sum_{\mathrm{j} \in \mathrm{J}} CC^j\ \mathrm{Q_D^j} + \mathrm{CC_R} \cdot \sum_{\mathrm{j} \in \mathrm{I}} Q^i\ \mathrm{x}\ 8000 \\ &+ \sum_{\mathrm{t} \in \mathrm{TE}} C_t\ \mathrm{MIND^t} + \mathrm{C_{WW}}\ Q_{Wtot}\ \mathrm{x}\ 8000 + \mathrm{C_{EN}}\ \frac{\mathrm{E_f}}{\eta_p \eta_m} \end{aligned} \tag{AII-44}$$

The capital costs (CC) are calculated by means of correlations recommended in (Wright & Woods, 1993), using an exponent (ICp) for RO, NF, ZnP and the reference values of costs and flow rates defined for this correlation. The CCs for units RO, NF and ZnP are given by:

$$CC^{RO} = \mathrm{IC}_{\mathrm{RO}} \left( \frac{\mathrm{Q}_{\mathrm{D}}^{\mathrm{RO}}}{16700} \right)^{\mathrm{IC}_{\mathrm{RO}}^{\mathrm{P}}} \tag{AII-45}$$

$$CC^{NF} = \mathrm{IC}_{\mathrm{NF}} \left( \frac{\mathrm{Q}_{\mathrm{D}}^{\mathrm{NF}}}{16700} \right)^{\mathrm{IC}_{\mathrm{NF}}^{\mathrm{P}}} \tag{AII-46}$$

$$CC_{ZnP} = \mathrm{IC}_{\mathrm{ZnP}} \left( \frac{\mathrm{Q}_{\mathrm{W,out}}}{5700} \right)^{IC_{ZnP}^{p}} \tag{AII-47}$$

For rinsing units the reference cost parameter $\mathrm{IC}_{\mathrm{R}}$ per rinsing unit is taken from (Thöming, 2002) and $\mathrm{CC}_{\mathrm{R}}$ is calculated as follows:

$$CC_{R} = \mathrm{IC}_{\mathrm{R}} \sum_{\mathrm{i} \in \mathrm{I}} Z^{i} \tag{AII-48}$$

**ECO module**

For attaining the environmental objectives in figures the amounts of the substances with potential environmental impacts are assessed by means of the supplementary data given in (LCA, 2001). This data set defines environmental impact categories (c) and conversion factors (CF) for certain substances(s). By means of these figures, the amount (mass indexes from mass balances) of potential environmental impacts can be converted into indicator values over a certain time horizon.

Mass Index (MIND) for the substances Ni, Zn, $CaOH_2$ and $H_2O$ are defined as follows:

$$MIND^{Ni} = \frac{(\mathrm{Y}_{0}^{\mathrm{Ni}} - \mathrm{X}_{out}^{1,\mathrm{Ni}}\ \mathrm{D} - \mathrm{X}_{C}^{\mathrm{NF,Ni}}\ \mathrm{Q}_{\mathrm{Recyel}}^{\mathrm{NF}}}{1000} = 8000 \tag{AII-49}$$

$$MIND^{Zn} = \frac{\mathrm{Q}_{\mathrm{W,out}}\, X_{W,out}^{Zn}}{1000} \mathrm{x}\ 8000 \tag{AII-50}$$

$$MIND^{CaOH_2} = \frac{\mathrm{X}_{\mathrm{M}}^{\mathrm{Zn}} Mwt^{CaOH_2}}{1000} \mathrm{\ x\ } 8000 \tag{AII-51}$$

$$MIND^{Wa} = (\mathrm{F}_{\mathrm{R}} + \mathrm{F}_{\mathrm{Bath}}) \mathrm{\ x\ } 1 \mathrm{\ x\ } 8000 \tag{AII-52}$$

The amount of resources consumed for total energy consumption within the system is calculated considering the country's specific distribution (%) of energy resources utilization for generating electricity and the related efficiency of the power station technology applied. Its contribution to $CO_2$ emissions is assessed by means of $CO_2$ emission's factor (kt/PJ) defined in (Lichtblick, 2002):

Mass index for energy resources which are soft coal (SC), hard coal (HC), natural gas (NG) and crude oil (CO):

$$MIND^{S} = \mathrm{E}_{\mathrm{tot}} \frac{FRAC^{S}}{0{,}28 \mathrm{\ x\ } 10^{3} \mathrm{\ x\ h}^{\mathrm{s}} WG^{S}} \quad \forall \mathrm{\ s} \tag{AII-53}$$

Where Etot is the total amount of energy used in kWh, Frac is the fraction of energy from the energy mixture of Germany in 2002, that is provided by energy resource s, $h^s$ is the heating value MJ/$m^3$ of s per kg, $WG^s$ is the efficiency of energy production using s and f is a conversion factor which converts MJ to kWh.

Environmental Impact Indicator value $IND^{c,s}$ for each indicator category related with considered substance:

$$IND^{C,S} = \mathrm{CF}^{\mathrm{C,S}} \mathrm{\ MIND}^{\mathrm{S}} \quad \forall \mathrm{c,s} \tag{AII-54}$$

C is the set of considered impact categories: C = human toxicity, fresh water aquatic toxicity, fresh water sediment, depletion of abiotic resources.

The $T_i$ value for each impact category is:

$$T_i^C = \sum_{s \in S} IND^{C,S} \quad \forall c \qquad \text{(AII-55)}$$

The relative value of environmental impact indicator for each indicator category is:

$$T_{i,\mathrm{Rel}}^C = \frac{\mathrm{T}_i^C}{\mathrm{T}_{i,\mathrm{Ref}}^C} \quad \forall c \qquad \text{(AII-56)}$$

The maximal relative value $T_{i,Rel,max}$ of environmental impact indicator out of all indicator category is:

$$T_{i,\mathrm{Rel,Max}} = \max_{c \in C}\left(\mathrm{T}_{i,\mathrm{Rel}}^C\right) \qquad \text{(AII-57)}$$

Multi-objective function (ZF) which integrates both eco-eco trade-off in a function is:

$$ZF = \alpha\,\mathrm{TAC} + \beta\,\mathrm{T}_{i,\mathrm{Rel,max}} \qquad \text{(AII-58)}$$

The minimization of the objective function ZF that is subject to the constraints which form the feasibility region is referred to a mixed-integer nonlinear program (MINLP). This is due to the non-linearity of Equations (AII-3), (AII-9), (AII-10), (AII-22), (AII-23), (AII-29) and (AII-30) and the binaries in the Equations (AII-6), (AII-7), (AII-13) and (AII-28).

The optimization problem here is to achieve an eco-optimal system structure, which comprises an optimal number of rinsing stages and an optimal arrangement of regenerators controlled with corresponding economic and ecological aspects. This integration of these eco-eco trade-offs in terms of TAC and Ti'max in a multi-objective function is represented in Eq.(2.20). The representative objectives in the objective function are outcomes of (a) mass and compound balances for compounds with potential environmental impacts (Eqs. (AII-1) to (AII-38), Eqs. (AII-39) to (AII-42) and Eqs. (AII-49) to (AII-57)), (b) the regenerator and rinsing unit specifications, like specific costs (Eq. (AII-5) and Eqs. (AII-43) to (AII-48)) and regenerator performances (Eqs. (AII-15), (AII-18), and (AII-25)) and (c) system parameterizations like flow rates of recycle streams. All these influences are represented in the case study by the equality constraints (Eqs. (AII-1) to (AII-5), (AII-8) to (AII-12), (AII-14), (AII-15), (AII-17) to (AII-20), (AII-22) to (AII-27), (AII-29) to (AII-38)) and by inequality constraints (Eqs. (AII-6), (AII-13), (AII-16), (AII-21), and (AII-28)). The existence of the units is controlled by binary variables (Eq. (AII-7)) and by flow rate limitation inequality (Eq. (AII-16)).

In mathematical programming, all system variables in optimization models should be properly initialized to achieve reasonable solutions. If not, MINLP problem is usually difficult to solve, since then it results in a discrete optimization problem (Grossmann & Kravanja, 1995). For example in this case study, when the max function is applied at initialization and n-Norm is used in model algorithm at the same time, the most sensitive indicator value differs from the value calculated by n-Norm, if $T_{i,Rel,max}$ value is $0 < T_{i,Rel,max} < 1$. This happens due to the contrary requirements of MINLP and DNLP.

The solution of the MINLP, modelled in GAMS, version 21.3 (GAMS, 2004) using the SBB solver, provides the unit interconnections, the flow rates and concentration of each stream in the superstructure and the number of rinsing stages.

## Nomenclature

### Sets and Set Elements

| | | |
|---|---|---|
| C | Set of impact categories c impact category | |
| index I | Set of rinsing stages | 1, 2, ..., $i_e$ |
| | $i$, $i_1$, $i_2$ : rinsing stage index | |
| | $i_e$ : Greatest element of I | |
| J | Set of concentrators (NF, RO) | |
| | $j$, $j_1$, $j_2$ : concentrator index | |
| S | Set of substances consumed<br>($Ni,Zn,CaOH_2,WA,SC,HC,NG,CO$) | |
| | s: Element of S | |
| TE | Set of trace elements (subset of S) ( $Ni,Zn,CaOH_2$) | |
| | t: Element of TE | |

### Variables and Constants

| | | |
|---|---|---|
| a | Annual depreciation | a |
| $CC_R$, $CC^j$, $CC_{ZnP}$ | Capital cost of rinsing units, concentrator unit j and zinc precipitation | EUR /a |
| $CF^{c,s}$ | Characteristic Factor for impact category c and substance s | |
| $C_R$, $C^j$ | specific operational costs for rinsing and concentrator unit j | EUR /kg water |
| $C_{WW}$, $C_{EN}$, $C_t$ | specific costs for substances | EUR /kg substance |
| D | Drag-out stream | kg/h |
| $DC_{Ratio}{}^j$ | Ratio : $Q_D$ / $Q_C$ for concentrator j | |

**Variables and Constants (*continued*)**

| | | |
|---|---|---|
| $E^j$, $E_F$, $E_P$, $E_{tot}$ | Energy consumption for concentrators, fresh water pumping, pumping and total energy consumption | Wh/a |
| $E_{spez,J}{}^j$ | Specific work for each concentrator | Wh/kg dilute |
| $E_{spezW,p}$ | Specific work for a centrifugal piston pump SpezW | Wh/kg |
| $F_R$, $F_{Bath}$ | Fresh water inflow to rinsing system and to process bath | kg/h |
| $h^s$ | heating value of substance | MJ/m^3 |
| $IC_J$, $IC_{ZnP}$, $IC_R$ | Reference capital cost of unit j, zinc precipitation and rinsing stages | EUR |
| $IC_J{}^p$, $IC_{ZnP}{}^p$ | Exponent of cost function for concentrator units and zinc precipitation | |
| $IND^{c,s}$ | Indicator value for impact category c and substance s | |
| $Mwt^t$ | Molecular weight of trace element t | kg/mole |
| $MIND^s$ | Mass of substance s | kg/a |
| OC | Operational costs | EUR /a |
| $Q_W{}^i$, $Q_{WC}{}^j$, $Q_{WD}{}^j$, $Q_{Wtot}$ | Waste water produced in Rinsing, in the concentrate and dilute streams of concentrators and total amount of waste water | kg/h |
| $Q_{W,in}$, $Q_{W,out}$, $Q_{SL}$ | Inlet, outlet and sludge flow rates in Zinc Precipitation Module | kg/h |
| $Q_S{}^{j,i}$, $Q_R{}^{i}{}_{1}{}^{,}{}^{i}{}_{2}$, $Q^i$, $Q_{SP}{}^{i,j}$ | Backflow of the concentrators to rinsing or from concentrators to rinsing and between the rinsing stages | kg/h |
| $Q_{max}$ | Flow rate limitation | kg/h |
| $Q_J{}^j$, $Q_C{}^j$, $Q_{Recycl}{}^j$, $Q_D{}^j$, $Q_{CC}{}^{j}{}_{1}{}^{,j}{}_{2}$ | Flow rates of concentrator inlets, concentrate stream,dilute stream, concentrator cross flows and recycling stream | kg/h |
| R | Rinsing criteria | |

## Variables and Constants (*continued*)

| | | |
|---|---|---|
| $SpF_{Ww}$ | Split factor for waste water from Precipitation stage | |
| $SplitF^{j,t}$ | Split factor for trace element t in the dilute stream of concentrator j | |
| TAC | Total annualized costs | EUR |
| $T_i^c$ | Environmental impact category indicator value | |
| $T_{i,Rel}^c$ (Ti′),<br>$T_{i,Rel,max}$ (Ti′max) | Relative value of $T_i^c$ and the maximum of them | |
| $T_{i,Ref}^c$ | Reference value for $T_i$ (for a 3 stage rinsing case) | |
| $WG^s$ | Efficiency of energy production for substance s | |
| $X_{in}^{i,t}$, $X_{out}^{i,t}$, $Y^{i,t}$, $Y_0^t$ | Concentration of rinsing inlet and outlet, drag-out stream after each rinsing stage and the initial drag-out concentration of substances t | g/L |
| $X_J^{i,t}$, $X_D^{j,t}$, $X_C^{j,t}$, $X_{SL}^t$ | Concentration of concentrator inlet, dilute and concentrate outflows and in sludge | g/L |
| $X_M^{Zn}$ | Molarity of Zn | g/mole |
| $X_{W,in}^{Zn}$ | Inlet concentration of Zn | g/L |
| $X_{W,out}^{Zn}$ | Outlet concentration of Zn | g/L |
| $z_{RO,z}^i$ | Binary variables for the existence of concentrators and rinsing stage i respectively | |
| ZF | Objective function | |
| α | Weighting factor for annual costs in the objective function | 1/€ |
| β | Weighting factor for environmental impacts in the objective function | - |
| $\eta_p$ | efficiency of pump | |
| $\eta_m$ | efficiency of motor | |

# LITERATURE

**Alva-Argaez et al., 1998**
Alva-Argaez, A.; Kokossis, A.C.; Smith, R. Wastewater minimisation of industrial systems using an integrated approach. Computers and Chemical Engineering, 1998, 22, 741-744.

**Angira & Babu, 2006**
Angira,R.; Babu,B.V. Optimization of process synthesis and design problems: A modified differential evolution approach. Chemical Engineering Science, 2006, 61, 4707-4721.

**Anonymous 1, 2003**
Anonymous 1: www.pfonline.com, 2003.

**Anonymous 2, 2003**
Anonymous 2: www.nickelforum-eura.org/index.cfm/ci_id/11853.htm, 2003.

**Azapagic, 1999**
Azapagic, A. Life cycle assessment and its application to process selection, design and optimization. Chem. Eng. J., 1999, 73, 1-21.

**Azapagic & Clift, 1999a**
Azapagic, A.; Clift, R. The application of life cycle assessment to process optimization, Computers and Chemical Engineering 1999, 23, 1509-1526.

**Azapagic & Clift, 1999b**
Azapagic, A.; Clift, R. Life cycle assessment and multiobjective optimization. Journal of Cleaner Production, 1999, 7, 135-143.

**Bagajewicz, 2000**
Bagajewicz, M..A review of recent design procedures for water networks in refineries and process plants. Comput.Chem.Eng., 2000, 24, 2093-2113.

**Bagajewicz et al., 2000**
Bagajewicz, M.J.; Rivas, M.; Salveski, M.J. A robust method to obtain optimal and sub-optimal design and retrofit solutions of water utilization systems with multiple contaminants in process plants. Computers and Chemical Engineering., 2000, 24, 1461-1466.

**Barnicki & Siirola, 2004**
Barnicki, S.D.; Siirola, J.J. Process synthesis prospective. Comput.Chem.Eng., 2004, 28, 441-446.

**Barnthouse, 1998**
Barnthouse, L. et al. Life Cycle Impact Assessment: The state-of-the-art. Pensacola, FL. Society of Environmental Toxicology and Chemistry (SETAC), 1998.

**Bedenik et al., 2004**
Bedenik, N.I.; Pahor, B.; Kravanja,Z. An integrated strategy for the hierarchical multilevel MINLP synthesis of overall process flowsheets using the combined synthesis/analysis approach. Computers and Chemical Engineering, 2004, 28, 693-706.

**Biegler et al., 1997**
Biegler, L.T.; Grossmann, I.E.; Westerberg, A.W. Systematic Methods of Chemical Process Design, Prentice-Hall PTR, New Jersey, USA, 1997.

**Biegler & Grossmann, 2004**
Biegler,L.T.; Grossmann, I.E. Retrospective on optimization. Computers and Chemical Engineering., 2004, 28, 1169-1192.

**Blass, 1997**
Blass, E. Entwicklung verfahrenstechnischer Prozesse. Methoden - Zielsuche - Lösungssuche - Lösungsauswahl. Springer-Verlag, München, Deutschland, 1997.

**Brouwer et al., 1999**
Brouwer, J-W; Kuhm, P.; Vier, J. Patent Application - DE 198 13 058 A 1. Deutsches Patent- und Markenamt, 1999.

**Burgess & Brennan, 2001**
Burgess, A.A.; Brennan, D.J. Application of life Cycle assessment to chemical processes, Chem. Eng. Sci., 2001, 56, 2589-2604.

**Cape, 1987**
Cape, T. W. ASM International Handbook Committee. Metals Handbook 9 th Edition, ASM International, USA, 1987,13, 383-388.

**Chen et al., 2002**
Chen, H.; Wen, Y.; Waters, M. D.; Shonnard, D. R. Design Guidance for Chemical Processes Using Environmental Economic Assessments. Ind. Eng. Chem. Res., 2002, 41(18), 4503-4513.

**Cohen & Overcash, 1995**
Cohen Hubal, E.A.; Overcash, M.R. Net-waste-reduction analysis applied to zero-water discharge systems for chromic acid electroplating, M.R. J. Cleaner Prod., 1995, 3, 161-167.

**Consoli et al., 1993**
Consoli, F. et al. Guidelines for life cycle assessment: A code of practice. Proceedings of a workshop in Sesimbra, Portugal. Pensacola, FL. Society of Environmental Toxicology and Chemistry (SETAC), 1993.

**Cushnie Jr., 1994**
Cushnie Jr., G.C. Pollution prevention and control technology for plating operations. Library of Congress Cataloging-in-Publication Data. MI, USA. National Center of Manufacturing Sciences (NCMS), 1994.

**Dantus & High, 1996**
Dantus, M.M.; High, K.A. Economic evaluation for the retrofit of chemical processes through waste minimization and process integration. Ind. Eng. Chem. Res., 35:4566-4578, 1996.

**Dantus & High, 1999**
Dantus,M.M.; High,K.A. Evaluation of waste minimization alternatives under uncertainty: a multiobjective optimization approach. Comput. Chem. Eng., 1999, 23, 1493-1508.

**Diwekar & Fu, 2004**
Diwekar, M.U.; Fu,Y. Cost effective environmental control technology for utilities. Advances in Enviromental Research, 2004, 8, 173-196.

**DIN EN ISO 14040, 1997**
DIN EN ISO 14040: Umweltmanagement, Ökobilanzen, Prinzipien und allgemeine Anforderungen, Ausgabe 1997-06, Beuth-Verlag, Berlin, Deutschland, 1997.

**Douglas, 1985**
Douglas, J. M. Hierarchical Decision Procedure For Process Synthesis. AIChE Journal, v 31, n 3, Mar, 1985, p 353-362.

**Edgar et al., 2001**
Edgar, T.F.; Himmelblau, D.M.; Lasdon,L.S. Optimization of Chemical Processes, McGraw-Hill: New York, USA, 2001.

**Ehrgott, 2005**
Ehrgott, M; Multicriteria Optimization. Springer, Heidelberg, Germany, 2005.

**El Halwagi, 1997**
El-Halwagi, M.M. Pollution Prevention through Process Integration, Academic Press, California, USA, 1997.

**EPA, 2000**
EPA/625/R-99/008. Approaching zero discharge in surface finishing. Capsule Report. 2000.

**Erol & Thöming, 2005**
Erol, P.; Thöming, J. ECO-Design of Reuse and Recycling Networks by Multiobjective Optimization. J. Cleaner Prod., 2005, 13, 1449-1460.

**Erol & Thöming, 2006**
Erol, P.; Thöming, J. ECO-Optimization of Pre-treatment Processes in Metal Finishing. Computers and Chemical Engineering Journal., 2006, 30, 587-598.

**Floudas et al., 1989**
Floudas, C.A.; Aggarwal, A.; Ciric, A.R. Global Optimum Search For Nonconvex Nlp And Minlp Problems. Computers & Chemical Engineering, V 13, N 10, Oct, 1989, P 1117-1132.

**Freeman, 1995**
Freeman, H.M. Industrial Pollution Prevention Handbook. McGraw-Hill, 1995.

**Frenser et al., 2007**
Fresner, J.; Schnitzer, H.; Gwehenberger, G.; Planasch, M.; Brunner, C.; Taferner, K.; Mair, J. Practical experiences with the implementation of the concept of zero emissions in the surface treatment industry in Austria. Journal of Cleaner Production., 2007, 15, 1228-1239.

**Futterer & Munsch, 1990**
Futterer, E.; Munsch, M. Flow-Sheeting-Programme für die Prozeßsimulation. Chem.-Ing.-Tech., 1990, 62, Nr. 1, 9-16.

**GAMS, 2000**
GAMS, Version 21.2. GAMS Development Corp. Washington DC, USA, 2001 http://www.gams.com, 2000.

**GAMS, 2004**
GAMS, Version 23.1. GAMS Development Corp. Washington DC, USA, 2004 (http://www.gams.com)

**Goedkoop et al., 1998**
Godekoop, M. ; Hofstetter, P.; Müller-Wenk, R.; Spriemsma, R. LCA Methodology : The Eco-Indicator 98 Explained. International Journal of LCA, 1998, 6, 352-360.

**Goedkoop & Spriensma, 1999**
Goedkoop, M.; Spriensma,R. The Eco-indicator99. A damage oriented method for life cycle impact assessment. Pre Consultants, Amersfoort, 1999.

**Grossmann, 1996**
Grossmann, I.E. Mixed-Integer Optimization Techniques for Algorithmic Process Synthesis. Advances in Chemical Engineering, 1996, 23, 171-246.

**Grossmann, 1999**
Grossmann, I.E. A systematic modeling framework of superstructure optimization in process synthesis. Comput.Chem.Eng., 1999, 23, 709-731.

**Grossmann et al., 2000**
Grossmann, I. E.; Caballero, J.A. and Yeomans , H. Advances in mathematical Programming for the synthesis of Process Systems. Latin American Applied Research, 2000, 30, 263-284.

**Grossmann & Biegler, 2004**
Grossmann, I.E.; Biegler,L.T. Part-II Future perspective on optimization. Computers and Chemical Engineering. 2004, 28, 1193-1218.

**Grossmann & Kravanja, 1995**
Grossmann, I.E.; Kravanja, Z. Mixed-integer nonlinear programming techniques for process systems engineering.Comp. Chem. Eng., 1995, 19, S189-S204.

**Grossmann & Sargent, 1979**
Grossmann, I. E.; Sargent, R.W.H. Optimum Design Of Multipurpose Chemical Plants. Industrial & Engineering Chemistry, Process Design and Development, 1979, v 18, n 2, Apr, p 343-348

**Han et al., 1991**
Han,S-Y.; Kim,T.J. ; Adigüzel,I. Integration of programming models and expert systems: An application to facility planning and management. Computers, Environment and Urban Systems, 1991, 15, 3, 189-201.

**Harmsen, 2004**
Harmsen, G.J. Industrial best practices of conceptual process design. Chemical Engineering and Processing., 2004, 43, 677-681.

**Higgins, 1995**
Higgins, T.E. Pollution Prevention Handbook. CRC Press, 1995.

**Holmes, 2002**
Holmes,D. Water and chemicals recovery in the German automotive industry. Membrane Technology, October, 2002.

**ISO, 1997**
ISO. Environmental management – Life cycle assessment 14040: Principles and framework, ISO office, Geneva, 1997.

**Karslı, 2004**
Karslı,G. Simulated Annealing for The Generation of Pareto Fronts with Aerospace Applications. MSc. Thesis, M.E.T.U., Ankara, Turkey, 2004.

**Khan et al., 2001**
Khan, F.I.; Natrajan, B.R.; Revathi, P. GreenPro: a new methodology for cleaner and greener process design. Journal of Loss Prevention in the Process Industries, 2001, 14, 307-328.

**Khan et al., 2004**
Khan,F.I.; Sadiq,R.; Veitch,B. Life cycle iNdeX (LInX): a new indexing procedure for process and product design and decision-making. Journal of Cleaner Production, 2004, 12, 59-76.

**Kheawhom & Hirao, 2004**
Kheawhom, S.; Hirao, M. Decision support tools for environmentally benign process design under uncertainty. Comput. Chem. Eng., 2004, 28, 1715-1723.

**Kjaerheim, 2005**
Kjaerheim, G. Cleaner production and sustainability. Journal of Cleaner Production, 2005, 13, 329-339.

**Kocis & Grossmann, 1987**
Kocis, G.R. ; Grossmann, I.E. Relaxation Strategy For The Structural Optimization Of Process Flow Sheets Industrial & Engineering Chemistry Research, 1987, v 26, n 9, Sep, p 1869-1880.

**Kocis & Grossmann, 1988**
Kocis, G.R.; Grossmann, I.E. Global Optimization Of Nonconvex Mixed-Integer Nonlinear Programming (Minlp) Problems In Process Synthesis. Industrial & Engineering Chemistry Research, V 27, N 8, Aug, 1988, P 1407-1421.

**Kocis & Grossmann, 1989a**
Kocis, G.R.; Grossmann, I.E. Computational Experience With Dicopt Solving Minlp Problems In Process Systems Engineering. Computers & Chemical Engineering, 1989 , V 13, N 3, Mar, P 307-315.

**Kocis & Grossmann, 1989b**
Kocis, G.R.; Grossmann, I.E. Modelling and Decomposition Strategy for The MINLP Optimization of Process Flowsheets. Computers & Chemical Engineering, 1989, V 13, N 7, Jul, P 797-819.

**Koeningsberger, 1986**
Koenigsberger, M. D. Preventing Pollution At The Source. Chemical Engineering Progress, 1986, v 82, n 5, May, p 7-9.

**Koppol et al., 2003**
Koppol, A.P.R.; Bagajewicz, M.J.; Dericks, B.J.; Salveski, M.J. On zero water discharge solutions in the process industry. Advances in Environmental Research, 2003, 8, 151-171.

**Kovacs et al., 2000**
Kovacs, Z.; Ercsey, Z.; Friedler, F.; Fan, L.T. Separation–network synthesis: global optimum through rigorous super-structure, Computers and Chemical Engineering, 2000, 24, 1881-1900.

**Kuo et.al, 1997**
Kuo, Wen-Chu J.; Smith, R. Effluent treatment system design. Chemical Engineering Science, 1997, 52, 23, 4273-4290.

**LCA, 2001**
LCA -An operational guide to the ISO standards, Final Report, Centre of Environmental Science-Leiden University (CML), May, 2001.
**http://www.leidenuniv.nl/interfac/cml/ssp/projects/lca2/lca2.html**

**Lens et al., 2002**
Lens, P.N.L.; Vallero, M.; Graciella, G.-G.; Rebac, S.; Lettinga, G. Environmental protection in industry for sustainable development. Water recycling and resource recovery in industry: Analysis, Technologies and Implementation', IWA-Publishings, 2002.

**Lewin et al., 2002**
Lewin, D.R.; Seider, W.D.; Seader, J.D. Integrated process design instruction. Computers and Chemical Engineering, 2002, 26, 295-306.

**Liao, 2005**
Liao,S-H. Expert system methodologies and applications - a decade review from 1995 to 2004. Expert Systems with Applications, 2005, 28, 93-103.

**Lichtblick, 2002**
Lichtblick,Strommix-Germany:
(http://www.lichtblick.de\/newsundinfos\/strommarkt_strommix), 2002.

**Linnhoff & Turner, 1981**
Linnhoff, B.; Turner, J.A. Heat-Recovery Networks: New Insights Yield Big Savings. Chemical Engineering (New York) , 1981, v 88, n 22, Nov 2, p 56-70.

**Mallick, 1996**
Mallick,S.K.; Cabezas,H.; Barc,J.C.; Sikdar,S.K. A Pollution Reduction Methodology for Chemical Process Simulators. Ind.Eng.Chem.Res., 1996, 35, 4128.

**Miettinen, 1999**
Miettinen, K.M. Nonlinear Multiobjective Optimization, Kluwer Academic Publishers, Massachusetts, 1999; p.78ff.

**Norris, 2001**
Norris, G.A. The requirement for congruence in Normalization. Int. J. LCA, 2001, 6:85-86.

**Perkins et al., 1996**
Perkins, J.D.; Sargent, W.H.R.; Vazquez-Roman, R.; Cho, J.H. Computer Generation of Process Models. Computers and Chemical Engineering, 1996, 20, 6/7, 635-639.

**Perry & Green, 1997**
Perry, R.H.; Green, D.W. Perry's Chemical Engineers' Handbook. 7th Edition. The McGraw-Hill Companies, New York, USA, 1997.

**Pistikopoulos et al., 1995**
Pistikopoulos, E.N.; Stefanis, S.K.; Livingston, A.G. A Methodology for Minimum Environmental Impact Analysis. AIChE Symp.Ser., 1995, 90, 139.

**Proos et al., 2001**
Proos, K.A. ; Steven, G.P. ; Querin, Q.M. ; Xie, Y.M. Multicriterion Evolutionary Structural Optimization Using the Weighting and the Global Criterion Methods. AIAA Journal, 2001, October, 39, Nr. 10, 1509-1526.

**Rausch, 1990**
Rausch, W. The Phosphating of Metals. Finishing Publications LTD. England, 1990.

**Rhinehart et al. ,1995**
Rhinehart, R.R.; Natarajan, S.; Anderson, J.J. A course in process dynamics and control. Chemical Engineering Education,1995, 29(4), 218-221.

**Rizzoli & Young, 1997**
Rizzoli, A.E.; Young, W.J. Delivering environmental decision support systems: software tools and techniques. Environmental Modelling \& Software, 1997, 12, Nr. 2-3, 237-249.

**Rossiter & Kumana, 1995**
Rossiter, A.P.; Kumana, J.D. In Waste Minimization through Process Design. McGraw-Hill, New York, 1995, 43-49. 225-229.

**Salcedo, 1992**
Salcedo, R.L.Solving Nonconvex Nonlinear Programming And Mixed-Integer Nonlinear Programming Problems With Adaptive Random Search. Industrial & Engineering Chemistry Research, 1992, Jan, v 31, n 1, , p 262-273.

**Salveski & Bagajewicz, 2000a**
Salveski, M.J.; Bagajewicz, M.J. On the optimality conditions of water utilization systems in process plants with single contaminants. Chemical Engineering Science, 2000, 55, 5033-5048.

**Salveski & Bagajewicz, 2000b**
Salveski, M.J.; Bagajewicz, M.J. Design of water utilization systems in process plants with a single contaminant. Waste Management, 2000, 20, 659-664.

**Salveski & Bagajewicz, 2001**
Salveski, M.J.; Bagajewicz, M.J. Algorithmic procedure to design water utilization systems featuring a single contaminant in process plants. Chemical Engineering Science, 2001, 56, 1897-1911.

**Salveski & Bagajewicz, 2003**
Salveski, M.J.; Bagajewicz, M.J. On the necessary conditions of the optimality of water utilization systems in process plants with multiple contaminants. Chemical Engineering Science, 2003, 58, 5349-5362.

**Sankara, 1996a**
Sankara Narayanan, T.S.N. Influence of Various Factors on Phosphatability - An Overview. Metal Finishing, 1996, 86-90.

**Sankara, 1996b**
Sankara Narayanan, T.S.N. Performance Evaluation of Phosphating Formulations in Continous Operation. Metal Finishing, 1996, 40-43.

**Schmidt et al., 2000**
Schmidt,M.; Rathjen,K.D.; Stollberg,C.; Schönfeder,I. Membrantrennverfahren für Aluminiumgalvanik-Prozessströme prozessintegriert aufbereiten. Metalloberfläche, Galvanotechnik, 2000, 54, 6, 28-30.

**Schultze & Marquaro, 1999**
Schultze,J.; Marquaro,K.-D. Patent Anmeldung/Offenlegungsschrift – de 197 43 933 a1. Deutsches Patent-und Markenamt, 1999.

**Seppälä, 1999**
Seppälä, J. Decision analysis as a tool for Life Cycle Impact Assessment. LCA Documents Vol 4: Eco-Informa Press (http://www.scientificjournals.com), 1999.

**Szafnicki, 2005**
Szafnicki, K.; Narce, C.; Bourgois, J. Towards an integrated tool for control, supervision and operator training – application to industrial wastewater detoxication plants. 2005, 13, 729-738.

**SETAC, 1993**
SETAC, Guidelines for Life Cycle Assessment: A Code of Practice. SETAC, Society for environmental toxicology and chemistry workshop, Sesimbra, Portugal, 1993.

**Shen, 1999**
Shen, T.T. Industrial Pollution Prevention. Springer, 2nd edition, 1999.

**Shonnard & Hiew, 2000**
Shonnard,D.R.; Hiew,D.S. Comparative Environmental Assessments of VOC Recovery and Recycle Design Alternatives for Gaseous Waste Stream. Environ. Sci. Technol., 2000, 34, 5222-5228.

**Siirola, 1996**
Siirola, J.J. Industrial applications of chemical process synthesis. Advances in Chemical Engineering, 1996, 23, 2-61.

**Sing, 1996**
Sing, K Ng; Model Formulation of Multiple Objective Problems, 1996. http://www.comp.nus.edu.sg/~yeogk/course/ic432/projects/ngks/proj.html

**Stephanopoulos & Westerberg, 1976**
Stephanopoulos, G.; Westerberg, A.W. Studies In Process Synthesis Em Dash 2. Evolutionary Synthesis Of Optimal Process Flowsheets Chemical Engineering Science, 1976, v 31, n 3, p 195-204.

**Stephenson & Blackburn, 1997**
Stephenson, R.L.; Blackburn, J.B. The industrial wastewater systems handbook. 1st edition.CRC, 1997.

**Thöming, 2002**
Thöming, J. Optimal Design of Zero-Water Discharge Rinsing Systems, Environ. Sci. Technol., 2002, 36, 1107-1112.

**Weng et al.,1998**
Weng, D.; Wang, R.; Zhang, G. Environmental Impact of Zinc Phosphating in Surface Treatment of Metals. Metal Finishing, 1998, 54-57.

**Wright & Woods, 1993**
Wright, D.G.; Woods, D.R. Evaluation of Capital Cost Data: Part 7: Liquid Waste Disposal With Emphasis on Physical Treatment .Can. J. Chem. Eng., 1993, 71, 575-590.

**Wright & Woods, 1995**
Wright, D.G.; Woods, D.R. Evaluation of Capital Cost Data: Part 9: Liquid Waste Disposal With Emphasis on Chemical Treatment .Can. J. Chem. Eng., 1995, 73, 546-561.