

## LOW WASTE TECHNOLOGY IN METAL INDUSTRY - TRENDS FOR THE EIGHTIES

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**Abstract** - Environmental protection by low waste technology is of growing importance for all process operations in the metal industry. The actual situation of low waste technology, the developments up to now and the trends for the eighties have been described, using metallurgy of zinc, pickling of semi-finished products, chemical machining, organic coating and electroplating as significant examples for the large variety of branches in this field. This short review is outlining many new procedures which can successfully help to substitute waste treatment and waste disposal by recycling and recovery of valuable materials.

### PREFACE

The term metal industry is comprising a large variety of different branches, beginning with metal winning and recovery, fabrication metallurgy, metal-working, and extending to manufacture of machines, vehicles, planes, electro-technical equipments and devices, electronics and innumerable other metal products, for which metal finishing and electroplating are indispensable process steps for high quality standards. From this wide scope of activities in the metal industry several metallurgical operations and diverse surface treatment techniques, specific for different branches, will be taken into consideration in this short review.

The trends for the eighties of low waste technology in metal industry can be more easily evaluated after having a close look at the actual situation in this field and a summary of the developments up to now.

Considering the demands of today, developments can be predicted under the proviso that technical progress in this field is highly dependent on the general economical situation which is effectively influenced by many factors like supply with energy and raw materials, restrictions by metal cartels, monetary and commercial policies, purchasing power and labour market and, altogether, the political situation in the world. An important supposition for these predictions to come true is that the technical developments in Europe can be continued as it has been in the past 30 years without troublesome problems and that international trade will not be restricted.

With these assumptions in mind it is possible to estimate with good reliability which developments will be certain, probable, undesirable or not. Several actual technical developments from different fields in metal industry will be referred to because they may exemplarily indicate these trends of low waste technology for the eighties.

### ACTUAL SITUATION

In metal industry considerable differences in technology can be observed dependent on expenditure for research and development, investment costs and plant life in the various branches. Metallurgical equipments are operated for long periods of time compared with e. g. installations for surface treatment in printed circuit board production or for electronic components.

In several cases new procedures could be applied already which meet the environmental demands of today and even severe ecological regulations.

In other technical fields long-lasting and extensive research work had been necessary for finding out alternative technologies.

Therefore, in the beginning of the eighties we can recognize that low waste technology has been realized in many cases already whereas in some branches new developments are still to be established.

#### Metallurgy of zinc

The following comments on metallurgy are concerning zinc as an example to illustrate a few aspects of low waste technology because zinc is one of the most important non-ferrous metals and is produced on a very large scale in many industrial countries.

Zinc is mostly produced from sulfide ores which are shipped to smelters as finely grained concentrates from ore dressing. The zinc ore is roasted to form zinc oxide and sulfur dioxide which is supplied to a sulfuric acid plant. Using the pyrometallurgical route, zinc oxide is reduced at high temperature, giving zinc vapor which is condensed to form zinc metal of prime western quality. This can be refined by distillation. The hydrometallurgical route consists of leaching the roasted zinc ore in sulfuric acid. The leach liquor is purified by chemical treatments, and in electrolytical cells zinc is deposited cathodically in high grade quality.

The exhaust gases of all process steps which are operating at high temperatures contain sulfur dioxide, metal fumes and fine dusts and are treated in gas cleaning installations. The flue dust is repeated into the production process but part of the impurities is escaping into the environment. In the hydrometallurgical zinc recovery process large amounts of insoluble residues and precipitates are produced which have to be dumped.

#### Pickling of semi-finished products

In the metalworking industry all over the world more than 200 million tons of low carbon steel strip have to be pickled every year. Because part of the strip has to be pickled at least twice in the course of manufacture, on the basis of an average thickness of 4 mm, the total sheet metal area to be pickled amounts to about 20 billion m<sup>2</sup> per year. Further pickling operations are necessary in wire and tube production. Also large amounts of non-ferrous metal sheet, wire and tube rounds, mainly copper and brass, have to be pickled. If necessary, a preceding degreasing operation is performed either by liquid or vapor solvent or by soak cleaning.

For pickling mostly large production lines are in operation, preferably using sulfuric or hydrochloric acid. For low waste technology, in many plants spent acids are regenerated. For reducing the water consumption water is used in countercurrent rinses. Waste water has to be treated and is discharged into the sewer. Exhaust gases and fumes are sucked off and cleaned in washers and absorbers.

#### Chemical machining

Chemical machining, in particular for sheet metal treatments and for printed circuit board manufacture, is a technology of growing importance. Today spray etching machines are mostly used. To some extent spent etchants are regenerated automatically, otherwise they are shipped to smelters for metal recovery. In modern installations for low waste technology spray rinsing modules are operated with countercurrent water flow, thus avoiding waste water, provided that evaporation of the etchant is sufficient.

#### Organic coating

In metal industry a very large variety of different methods for applying organic coatings is necessary to meet all product requirements. In this short review it is impossible to discuss the pros and cons of these various paint systems as well as painting equipments. But generally, environmental protection has been highly improved by using modified paint systems in combination with automatic processing units.

#### Electroplating

In the field of electrolytic surface treatments we observe a complete change-over of technology beginning at the end of the seventies. Several years ago

plant design had mainly been determined by the aim of low surface finishing costs. Waste water had to be treated with chemicals, and its volume had been largely disregarded. In new installations, however, much attention is given to rinsing techniques and recycling processes directed towards low waste technology. In old plants we find very few rinsing steps resulting in high water consumption and severe problems caused by waste treatment regulations.

As drag-out of soak cleaners leads to a high chemical oxygen demand of waste water, efforts are made to return rinse water into the cleaning tank and to regenerate the cleaning solution. Spent pickling acids until now are mostly neutralized with hydroxyl ions forming large amounts of sludges. Drag-out of plating solutions necessitates waste water to be expensively treated.

Several modern plating installations are equipped with evaporators or volatiliziers already by which the volumes of the treating solutions are reduced in such a way that the rinse water can be completely returned into the tanks for water make-up. In this way waste has been avoided.

In older plating plants, however, large amounts of plating chemicals are consumed and high costs are arising for clean water supply, waste water treatment, waste water disposal, sludge shipment to a dump and depositing charges. Therefore, low waste technology is not only a question of governmental regulations but also commercial considerations.

#### DEVELOPMENTS UP TO NOW

Low waste technology is not a new idea but has long tradition, e. g. in metallurgy. In some cases secondary materials even are contributing to the economic operation of the smelters. In other fields of metal industry waste had been neglected for a long time, e. g. the metal content of hydroxyde sludges or spent solutions, water for cooling, rinsing or processing etc. Today environmental protection calls for low waste technologies, nobody had been thinking about several years ago.

#### Metallurgy of zinc

Zinc had been produced for many years in furnaces, each containing several hundred small horizontal retorts and condensers which could only be operated discontinuously. A half century ago, new vertical retort processes for continuous recovery had been developed. Today zinc is also produced in electrically heated furnaces and in shaft furnaces together with lead. The primary metal from all these pyrometallurgical processes is containing impurities, large amounts of process gases have to be treated, and the labour costs related to the zinc output are rather high.

Therefore, alternative hydrometallurgical routes have been tried out since exactly 100 years ago, and beginning in 1915, electrolytic zinc recovery processes have gained growing importance. Today, 75 percent of all zinc are produced by electrolytic processes. The overall yield of zinc and accordingly the zinc content and the properties of the residues to be dumped are highly dependent on the leaching procedure. Iron bearing sludges can contain the iron in form of goethite, jarosite or hematite, the latter can be utilized in a steel mill thus contributing to low waste technology.

#### Pickling of semi-finished products

In former times pickling with sulfuric acid at elevated temperatures had been cheaper than using hydrochloric acid at ambient temperature. Due to altered costs for acids and energy and development of regeneration systems for spent hydrochloric acid this pickling solution has been preferred during the last years. Addition of inhibitors to the acids can further decrease acid consumption. Another aspect is the sulfate content of effluents causing severe corrosion in drain pipes made of concrete.

#### Chemical machining

In chemical machining ferric chloride etchants had been preferred for a long time, and also ammoniumpersulfate had been widely used. In the meantime ferric chloride brings about advantages only if the spent etchant can be reoxidized by chlorine gas. Ammonium ions are substituted by sodium ions in persulfate etchants in order to avoid complexing of metals. Improvements also concern undercutting of the flanks. Etching machines are partly operated with auto-

matic control and for low waste technology closed loop rinsing systems find growing acceptance.

#### Organic coating

Many new developments have been accomplished in organic coating of metals during the last two decades, mostly under the aspect of low waste technology: Application of water containing paints or high solids has diminished the content of toxic chemical compounds in exhaust gases from baking ovens. Other important techniques for organic finishing have been electropainting, electrostatic spraying, electrostatic powder coating and coil coating. Further progress towards protection of the environment has been made by radiation curing of paints.

#### Electroplating

Thirty years ago in electroplating shops effective waste treatment procedures had not been commonly known. Later on large volumes of waste water had been treated in continuous flow-through installations, and for smaller amounts of waste water batch treatment had been applied.

Twenty years ago the first ion exchange plants for water recirculation had been set in operation and in this way water had been reclaimed up to 99 percent. The economy of this technology had been effectively supported by rising water supply costs and improved rinsing techniques. Further improvements with respect to low waste technology had been achieved by using separate ducts for individual waste water treatment.

During the last few years improved rinsing and reclaim techniques, mainly in new installations, have brought about remarkable progress towards avoiding of waste water and sludges.

### TRENDS FOR THE EIGHTIES

Low waste technology is the only real answer to the increasing requirements of environmental legislation. Instead of waste treatment and waste disposal new technologies for waste avoidance are the challenges of today. They can meet the demands for economic use of raw materials and energy in the future and contribute to the efficiency of our industries.

We can be sure that environmental regulations will be more restrictive in the future, that the expenditure for waste disposal and water supply as well as for energy, materials and labour will be increasing and that internal recycling processes will become indispensable tools for successful industrial operations.

It can be expected that surface technology in metal industry will become more and more important for durability of valuable industrial products, but that certain processes utilizing e. g. cadmium, chromic acid, mercury, cyanide etc. might only be tolerated in conjunction with closed loop recycling systems. In the relationship of costs for energy, materials and labour and in the rates of currency exchange substantial variations are possible which certainly will lead to technological consequences. These imponderabilities could be additionally affected by a shortage of energy or important raw materials.

On the other hand it would be very desirable if the development of economically operating waste avoiding processes could be sustained more effectively. Then in many cases low waste technology would soon be preferred without the threat of environmental legislation.

Low waste technology in the eighties will more and more be directed towards material recycling and waste heat recovery which will essentially contribute to economy. Progress in electronics and development of new sensors will facilitate automatic control of closed loop processes. Rising costs for materials and waste disposal and lower limitations of all emissions will effectively increase the need for improved installations. Rinsing time has to be adopted to the concentration ratio between adherent solution and rinse water. Treatment chemicals will be improved with regard to impurity build-up, and toxic compounds will be substituted by less harmful constituents.

### Metallurgy of zinc

Environmental protection in plants for pyrometallurgical zinc recovery is very difficult and expensive whereas in hydrometallurgy many problems like dust losses, escaping of sulfur dioxide, flue dust and metal fumes are avoided, and due to the better selectivity of chemical reactions at low temperatures high grade zinc can be directly deposited. The overall efficiency of hydro-metallurgical zinc recovery is better than in the pyrometallurgical route, and therefore, it is a convincing example for low waste technology.

Further approach towards low waste technology in hydrometallurgy of zinc will be made by pressure leaching of zinc sulfide ore. In this process step sulfide sulfur is oxidized only to elemental sulfur and sulfur dioxide cannot escape into the environment.

### Pickling of semi-finished products

In the eighties for pickling of steel strip flow and shallow-tank pickling plants will be preferred. Spent hydrochloric acid can be regenerated by oxidizing hydrolysis, using a fluidized bed, a turbulence chamber or a spray roasting furnace for the reaction. Each reactor brings about specific advantages. From the fluidized bed reactor the ferric oxide can be discharged as granulated material. In this way iron hydroxide sludges formed by chemical treatment of spent pickles will be avoided.

For pickling of copper, sulfuric acid has proven successfully because both copper and the pickling acid can be recovered electrolytically. Also rinse water can be recycled in a closed loop. This is also valid for pickling in chromic acid which can also be reoxidized by an electrolytic procedure.

Also for pickling of steel electrolytic treatments are expected to gain more attention due to better process control and lower environmental stresses. Furthermore, automatic mechanical descaling can help to cut costs.

### Chemical machining

For chemical machining in the eighties hydrogen peroxide as an oxidizing agent will become more important due to improved stabilizing agents especially for sulfuric acid spray etchants. Etchants for chemical machining will also be regenerated electrolytically as far as the type of etchant will allow it. Such a process does not only contribute to low waste technology but is also ensuring constant etching rates.

For low waste technology of alkaline etchants reduction of copper with hydrogen at elevated temperatures may become more important because in this way etchant regeneration can be accomplished.

### Organic coating

For organic finishing in the eighties further progress can be expected concerning reduced solvent contents and substitution of solvents by water, respectively. Improved application procedures will certainly contribute to low waste technology as the close cooperation between paint and lacquer industries and producers of painting installations will be continued. The properties of coating powders have been improved and production capability of materials for electrostatic powder coating can meet growing demands very fast.

Coil coating is offering another good chance for low waste technology in the eighties. The production rate of 136.5 million m<sup>2</sup> of coil coated steel sheet and of 75.0 million m<sup>2</sup> of coil coated aluminium sheet in Europe in 1978 is indicating the high capacity of this finishing industry.

Among the wide scope of developments in paint application, energy saving will attain growing importance. Therefore, paint curing by electron beams, continuous or pulse rays of ultraviolet light instead of heat can contribute to this aim.

### Electroplating

In electroplating much progress can be expected for low waste technology in the eighties because many chances for avoidance of waste are not being used up to now. Instead of treating waste water, application of less toxic plating solutions, sufficient time for draining over the plating tank, short spray

rinsing of the racked articles still over the treatment bath, and repeated immersion or spray rinsing with water counterflow has proven so effective that the volume of rinse water can nearly be neglected.

The small volumes of rinse water should no longer be treated with chemicals. Physical processes like membrane filtration or evaporation can easily adjust the water balance in such a way that the drag-out losses can completely be repeated. In this way also the problems of sludge disposal do no longer exist.

Therefore, low waste technology of surface treatment processes can mainly be attained by use of modern installations without fundamental variations of the chemistry. Attention is only necessary for avoiding impurity build-up in the solutions.

In electroplating closed loop rinsing systems in combination with copper, nickel, chromium, cadmium, brass, silver and gold deposition have proven successfully during the last few years and will become an indispensable equipment of every new plating installation. Regeneration of soak cleaners, e. g. by membrane filtration, and of pickling acids, e. g. by oxidizing hydrolysis, and of post treatment solutions, e. g. by ion exchange, will reduce waste to a minimum. Therefore, we can expect that at the end of the eighties toxic sludges from plating plants will belong to the past.

#### CONCLUSION

The trends for the eighties for low waste technology in the metal industry can be summarized with a few words: Instead of curing environmental stresses as a result of waste treatment attempts our aim must be to avoid waste as far as possible. And we have good chances to succeed because a large variety of low waste processes has been developed during the last few years. Therefore, the trends for the eighties should read as follows:

"From low waste technology to no-waste technology".