INDUSTRIAL LIQUID EFFLUENTS

iLE

A Guide Book on the Treatment of Effluents from the

Mining/Metallurgy
Paper
Plating
and
Textile

Industries

Edited by

Michael Cox
Pascal Négré
Lourdes Yurramendi

Edited by:
Prof. Michael Cox - University of Hertfordshire (United Kingdom)
Mr. Pascal Negré - IPM^2 (France)
Dr. Lourdes Yurramendi - INASMET-Tecnalia (Spain)

A publication of INASMET-Tecnalia
Paseo Mikeletegi, 2
Parque Tecnológico
E-20009 Donostia – San Sebastián – SPAIN

ISBN: 84-95520-14-1
D.L.: SS-1507/06

Printed by:
Michelena artes gráficas - Astigarraga (Gipuzkoa)

A Guide Book on the Treatment of Effluents from the Mining/Metallurgy, Paper, Plating and Textile Industries

Published by

inasmet
tecnalia

On behalf of the European Commission

ACKNOWLEDGEMENTS

Thanks are due to the European Commission for funding
the Industrial Liquid Effluents (ILE) Network under contract:
GIRT-CT-2002-05097, and to **Dr. Alain Adjemain**,
EC DG Research, Directorate Industrial Technologies,
for helpful advice and guidance during the term of the contract.

GENERAL INDEX

Section 1

Foreword

CONTENTS

I.

INTRODUCTION

This Guide book is final outcome of an EU funded Network on Industrial Liquid Effluents “ILE” initiated in 2001. Before detailing the results and conclusions from these studies it is appropriate to describe the background of the project.

Industry is using water in large quantities during production for cooling, cleaning and other requirements. This activity threatens our water resources due mainly to the discharge of pollutants into surface water. Therefore is essential to treat such effluents to avoid or reduce their environmental impact.

The industrial sectors involved in activities that produce liquid effluents are very extensive, and include general engineering processes such as plating, the use of cutting oils and burring, and more specific industries concerned with textiles, paper, mining and metallurgy. Each has their own specific problems and thus their own knowledge and expertise in the treatment of their effluents. On the other hand the number of commercially available technologies to treat liquid effluents is very wide and in addition there are also a number of emerging technologies. Sometimes there is not a good relationship between the needs of industry, the available technologies, and the innovative processes. For this reason it is essential to encourage all the parties concerned in the treatment of effluents to share information and to collaborate with each other. It is in this context that co-ordination of research, production, marketing, and services requires the intensive use of communication networks.

The number of associations and networks related to water treatment is very extensive and varied. They respond to diverse objectives and often have social or commercial aims in addition to scientific and technical purposes.

Taking all these considerations into account the ILE network was conceived to achieve the following specific objectives:

1. To group a number of European projects, universities, technical centres and laboratories having as a common link their expertise in the treatment of industrial aqueous effluents and to select, with the concerned industries, the best available techniques for treatment and recycling.
2. To add partners outside the European community to increase such treatment and recycling knowledge.
3. To create brainstorming groups on those emerging effluent treatment technologies that could be used in the future.

The main innovation of ILE Network compared to other networks is the contribution to the selection of the best available techniques (BATs) concerning the textile, plating, mining/metallurgy, and paper industries. Each of these four sectors has generated its own Cluster within the Network, very much linked to the relevant BREF (BAT reference document) of the IPPC Directive (Integrated Pollution Prevention and Control) described in detail later in this guide. In short, the IPPC Directive is concerned with minimising pollution from various industrial sources throughout the European Union and operators of industrial installations are required to obtain authorisation for compliance with the Directive from authorities in the EU countries, with in total about 50,000 installations involved.

New installations, and existing installations which are subject to “substantial changes”, have been required to meet the requirements of the IPPC Directive since 30 October 1999, with other installations brought into compliance by 30 October 2007. This is the key deadline for the full implementation of the Directive.

The IPPC Directive is based on several principles, namely (1) an integrated approach, (2) best available techniques, (3) flexibility, and (4) public participation.

1. The integrated approach means that the permits must take into account the whole environmental performance of the plant, covering emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, and restoration of the site upon closure. Thus the purpose of the Directive is to ensure a high level of protection of the environment taken as a whole.
2. The conditions of the permit include emission limiting values (ELVs) based on Best Available Techniques (BAT) , as defined in the IPPC Directive. To assist the licensing authorities and companies to determine BAT, the Commission organises an exchange of information between experts from the EU Member States, industry and environmental organisations. This work is co-ordinated by the European IPPC Bureau of the Institute for Prospective Technology Studies at the EU Joint Research Centre in Seville (Spain). This results in the adoption and publication by the Commission of BAT Reference Documents (BREFs**).** Executive summaries of the BREFs are also translated into the official EU languages.
3. The IPPC Directive contains elements of flexibility by allowing the licensing authorities, in determining permit conditions, to take into account:
    (a) the technical characteristics of the installation,
    (b) its geographical location, and
    (c) the local environmental conditions.
4. The Directive ensures that the public has a right to participate in the decision making process, and to be informed of its consequences, by having access to:
    (a) permit applications in order to provide comments,
    (b) permits,
    (c) results of the monitoring of releases, and
    (d) the European Pollutant Emission Register (EPER)**.**

> In the EPER, emission data reported by Member States are made accessible in a public register, which is intended to provide environmental information on major industrial activities. EPER will be replaced by the European Pollutant Release and Transfer Register (E-PRTR) from the 2007 reporting period onwards.

The discussion forums to select the BATs for particular industrial sectors, have involved all those concerned in the treatment of liquid effluents including research centers, industrial operators, universities, engineering practices, and consultants. The various forums not only provided dynamic collaboration and the dissemination of knowledge but also implemented a guide allowing the choice of the best technologies following considering of their advantages and disadvantages.

BATs are not static but in permanent evolution, as seen during the 4-year duration of this Network, as new technologies arise to provide better quality effluents without excessive costs. Therefore the signatories to the IPPC Directive are instructed to consider the development of new emerging techniques for clean-up and recycling.

This Thematic Network has been a tool for manufacturers keen to progress in the field of environmental protection. At the conclusion of the ILE Network, this Guide Book of waste-water treatment technologies includes information on the existing technology, applications, and technico-economic analysis allowing informed choices to be made. Regarding emerging technologies, the Guide gives a qualitative appreciation and an opinion on possible future applications. Thus it advises industrial concerns especially SMEs on choices for treating their liquid effluents, bearing in mind that one technology does not provide all answers because of individual and plant specific factors.

II.

INTEGRATED POLLUTION AND PREVENTION CONTROL DIRECTIVE (IPPC) 96/61/EC (24 September 1996)

INDEX

II.1. INTRODUCTION

The objective of this book is not to transcribe completely the IPPC Directive, which can be found easily on the Web (http://europa.eu.int/comm/environment/ippc), but to supply the reader with some explanations and clarifications on:

- its purpose,
- the considerations which led the Commission to propose it,
- tools for defining the limiting values of emission of pollutants, i.e. Best Available Techniques (BATS).

This work on BATS required the implementation of a specific office, the European Integrated Pollution Prevention and Control Bureau (http://eippcb.jrc.es) in Seville, Spain in charge of collecting the technical elements from experts of the Member States, and from industry and environmental organizations on the 30 sections of industry concerned by the Directive.

All the techniques used by every industrial sector were comprehensively considered and compiled and were assessed according to their performance. When they met the BATS criteria, they were used to define the limiting values for emission.

Several years work were necessary to collect all the required information and to establish, for each industrial sector, a BATS reference document (BREF) for the use of the proper authorities of Member States to deliver operational permits.

The Directive contains 23 articles describing the fields of application, certain of these articles are summarised below in detail:

Articles 4, 5, 6, 9, 12, 13 relate to the delivery of operational permits;
Article 18 concerns limiting values of emission.

The Directive also contains the following five appendices:

Annex 1: Categories of industrial activities covered by the Directive;
Annex 2: List of Directives quoted in the Articles;
Annex 3: Indicative List of the main polluting substances to be taken into account, if relevant, for fixing limiting emission values into air and water;
Annex 4: Considerations to be taken into account for determining the best available techniques (BATS);
Annex 5: Participation of the public in decision-making processes.

The Directive does not contain details of the limiting values of emission for those substances contained in Annex III, as these depend on BATS which themselves are subject to periodic re-evaluation. Other local considerations should also be taken into account in the fixing limiting emission values.

Finally, the limiting values with which companies will need to comply will depend on one hand on BATS, and on the other hand on the technical characteristics of the industrial installations, their geographical location, and local environmental conditions.

It is however foreseen in Article 18 that, on proposals from the Commission, the Council will fix limiting community emission values in accordance with procedures foreseen by the treaty for the categories of installations and the polluting substances aimed in Appendices I and III of the Directive.

The list of BREF completed or current on July 30, 2005 is attached to the this document.

II.2. WHY THE NEED FOR AN EUROPEAN DIRECTIVE ON THE CONTROL OF POLLUTION?

The Commission considered that:

1. The current European models of production and consumption do not correspond to the ethics of a sustainable development although important progress has been made over the last decades.
2. Industry is responsible for the major part of pollution and it has to make efforts to eliminate or limit the production of waste or pollutants.
3. It is easier to change the production models of some 20,000 industrial companies than to change the consumption patterns of a 100 million citizens of the European Union.
4. The ceaseless movements of companies from one part of Europe to another to find less binding operating conditions are abnormal.

Thus the Commission decided to create a Directive relating to the management and control of pollution from European industrial sites: Directive IPPC (Integrated Pollution Prevention and Control) 96 / 61 / EC, September 24, 1996.

During the creation of the Directive in 1996, the term “sustainable development” was not used nor had entered into use by the general public, but already in the mind of the Commission, the concept of environmental protection, and the concern of employees and more generally the public over the presence of dangerous substances in water, air, and waste was taken into account.

Furthermore, recommendations for the conservation of natural resources (water, energy, etc.) appeared in the Directive. One can therefore say that from its creation this Directive, established the ideas of *sustainable development*.

II.3. THE OBJECTIVE AND TOOLS OF THE IPPC DIRECTIVE

The IPPC Directive has as its objective the prevention and control of pollution generated by the industrial installations within the European Community.

It foresees measures aiming to avoid and, when that proves to be impossible, to reduce the emissions from the activities listed in Annex III into the air, water, and ground, including measures concerning waste, to reach a generally high level of environmental protection, and this without prejudice to Directive 85/337/EEC and other Community rules on such matters.

II.3.1. Best Available Techniques

To monitor and to control such pollution, limiting emission values are defined based on Best Available Techniques (BATS) which should in place at industrial sites in order to obtain an operational permit. Such permits will be supplied by the proper authorities of the Member States.

As too strict an introduction of Best Available Techniques, although providing a radical improvement to companies' environmental management, would risk putting a large number of them in danger, the Directive grants a delay of 11 years from the date of application of the Directive (14th October 1996) to set up the necessary BATS. This delay period thus ends in October 2007.

As noted above the Directive contains 23 articles covering fields of application and four appendices.

To fully understand specific terms used in the Directive, the main terms are defined below:

"*Limiting emission value*": the mass, expressed according to certain specific parameters, concentration and/or level of a emission, that may not be exceeded during one or more given periods. The limiting emission values may also be fixed for certain groups, families or categories of substances.

Limiting emission values of substances are generally applicable at the point of emission from an exit of the installation, with any possible dilution being excluded in their determination. As regards indirect emission into water, the effect of a water-treatment plant can be considered when determining the limiting emission values of an installation, on the condition that an equivalent level of protection is guaranteed for the environment in general and providing this does not lead to higher polluting levels in the environment, without prejudice to the Directive 76/464/EEC and the Directives adopted for its application.

"*Best Available Techniques (BAT*S)": the most effective and advanced development of activities and their methods of operation; that demonstrate the practical suitability of particular techniques to provide the means to comply with the limiting emission values, or when this is impossible, generally to reduce emissions and the overall impact on the environment.

In the context of this document:

> *“techniques”*, is meant the technologies used as well as the way by which the installation is designed, built, maintained, used and decommissioned;
>
> “*available*”, means such techniques that allow them to be applied in a particular branch of industry, under economically and technically viable conditions, considering costs and advantages, whether or not such techniques are used or produced in the territory of the interested Member’s State, and as far as the operator is concerned is reasonably accessible;
>
> *“best”,* shall mean the most effective techniques that in general can reach a high overall level of environmental protection;
>
> *“permit”*, shall mean part or all of one or several written decisions giving the operator the right to apply them to all or part of an installation under certain conditions that guarantees the installation satisfies the requirements of this Directive. A permit can be valid for one or several installations or parts of installations situated on the same site and operated by the same operator;
>
> *“proper authorities”*, one or several authorities or bodies responsible under the legislation of Member States, to carry out the obligations arising from this Directive.

The European IPPC office based in Seville (Spain) coordinates the work of the different persons in charge of BATS, and in addition the European Commission organizes exchanges of information among the experts of the Member States, industry and environmental organizations.

II.3.2. BREF (BATS Reference Document)

BREFs are the reference documents for the authorities responsible for delivering “integrated” licenses for exploitation, where “integrated” means that the total environmental performance of the industrial site must be taken into account: i.e. gas emissions, liquids, muds, raw materials, energy, noise, accident prevention, risk managment, etc.

Such authorities should also take into account:

1. the technical characteristics of the operations,
2. their geographical location, and
3. the local environmental conditions.

For every branch of industry a delay of two years has been granted to prepare the draft BREF, with all BREFs to be completed by the end of 2005.

Understanding that the public needs information about polluting industrial sites, the Directive has set up an European register of polluting emissions (EPER). In this register, that is available to the public, industrial sites exceeding the emission standards fixed by the Directive for polluting materials are recorded.

II.3.3. Application of the IPPC Directive

The “former”15 Members States of the European Union were allowed until October 1999 to amend their national legislation to conform with the Directive, while the “new” 10 Member States had to accept it at their date of entry in May 2004. But, as several “former” Members States had not complied by their due date, May 2004 was finally fixed for all the 25 States. However certain Members still have not completed the legislation to comply with the Directive.

For new installations the Directive has applied since October 1999, but for installations existing before the Directive was agreed, a period of 8 years was granted for their installations to conform with the standards.

II.3.4. Which Member States are covered?

The same rules apply to the “former” 15 members; while the four new members (Poland, Slovenia, Slovakia, and Latvia) have a period of longer transition (2008-2012) to install BATS in certain very specific installations. Bulgaria and Romania have also asked for periods of transition.

II.3.5. List of articles concerned with the licensing conditions for installations

Article 4 - Permits for new installations:

Member States shall take the necessary measures to ensure that no new installation is operated without a permit issued in accordance with this Directive, without prejudice to the exceptions provided in Council Directive 88/609/EEC of 24 November 1988 on the limitation of emissions of certain pollutants into the air from large combustion plants (12).

Article 5 - Requirements for the granting of permits for existing installations:

1. Member States shall take the necessary measures to ensure that the competent authorities, by means of permits in accordance with Articles 6 and 8 or, as appropriate, by reconsidering and, where necessary, by updating the conditions, that existing installations operate in accordance with the requirements of Articles 3, 7, 9, 10, 13, the first and second indents of 14, and 15 (2) not later than eight (8) years after the date on which this Directive is brought into effect, without prejudice to specific Community legislation.
2. Member States shall take the necessary measures to apply the provisions of Articles 1, 2, 11, 12, 14, third indent, 15 (1), (3) and (4), 16, 17 and 18 (2) to existing installations as from the date on which this Directive is brought into effect.

Article 6 - Applications for permits:

1. Member States shall take the necessary measures to ensure that an application to the competent authority for a permit includes description of:

- the installation and its activities,
- raw and auxiliary materials, other substances and the energy used in or generated by the installation,
- the sources of emissions from the installation,
- the conditions of the site of the installation,
- the nature and quantities of foreseeable emissions from the installation into each medium as well as identification of significant effects of the emissions on the environment,
- the proposed technology and other techniques for preventing or, where this not possible, reducing emissions from the installation,
- where necessary, measures for the prevention and recovery of waste generated by the installation,
- further measures planned to comply with the general principles of the basic obligations of the operator as provided for in Article 3,
- measures planned to monitor emissions into the environment.

An application for a permit shall also include a non-technical summary of the details referred to in the above indents.

2. Where information supplied in accordance with the requirements provided for in Directive 85/337/EEC, or a safety report prepared in accordance with Council Directive 82/501/EEC of 24 June 1982 on the major-accident hazards of certain industrial activities, (13) or other information produced in response to other legislation, fulfils any of the requirements of this Article, that information may be included in, or attached to, the application.

Article 9 - Conditions of the permit:

1. Member States shall ensure that the permit includes all measures necessary for the granting of permits in order to achieve a high level of protection for the environment as a whole by means of protection of the air, water, and land.
2. In the case of a new installation or a substantial change where Article 4 of Directive 85/337/EEC applies, any relevant information obtained or conclusion arrived at pursuant to Articles 5, 6 and 7 of that Directive shall be taken into consideration for the purposes of granting the permit.
3. The permit shall include emission limit values for pollutants, in particular, those listed in Annex III, likely to be emitted from the installation concerned in significant quantities, having regard to their nature and their potential to transfer pollution from one medium to another (water, air, and land). If necessary, the permit shall include appropriate requirements ensuring protection of the soil and ground water and measures concerning the management of waste generated by the installation. Where appropriate, limiting values may be supplemented or replaced by equivalent parameters or technical measures.

4. Without prejudice to Article 10, the emission limiting values and the equivalent parameters and technical measures referred to in paragraph 3 shall be based on the Best Available Techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit shall contain provisions on the minimization of long-distance or trans-boundary pollution and ensure a high level of protection for the environment as a whole.
5. The permit shall contain suitable release monitoring requirements, specifying measurement methodology and frequency, evaluation procedure, and an obligation to supply the competent authority with data required for checking compliance with the permit.
6. The permit shall contain measures relating to conditions other than normal operating conditions. Thus, where there is a risk that the environment may be affected, appropriate provision shall be made for start-up, leaks, malfunctions, momentary stoppages, and definitive cessation of operations.
7. The permit may also contain temporary derogations from the requirements of paragraph 4 if a rehabilitation plan approved by the competent authority ensures that these requirements will be met within six (6) months and if the project leads to a reduction of pollution.
8. The permit may contain such other specific conditions for the purposes of this Directive as the Member State or competent authority may think fit.
9. Without prejudice to the obligation to implement a permit procedure pursuant to this Directive, Member States may prescribe certain requirements for certain categories of installations in general, binding rules instead of including them in individual permit conditions, provided that an integrated approach and an equivalent high level of environmental protection as a whole are ensured.

Article 12 - Changes by operators to installations:

1. Member States shall take the necessary measures to ensure that the operator informs the competent authorities of any changes planned in the operation of the installation as referred to in Article 2 (10) (a). Where appropriate, the competent authorities shall update the permit or the conditions.
2. Member States shall take the necessary measures to ensure that no substantial change in the operation of the installation within the meaning of Article 2 (10) (b) planned by the operator is made without a permit issued in accordance with this Directive. The application for a permit and the decision by the competent authority must cover those parts of the installation and those aspects listed in Article 6 that may be affected by the change. The relevant provisions of Articles 3 and 6 to 10 and Article 15 (1), (2) and (4) shall apply mutatis mutandis.

Article 13 - Reconsideration and updating of permit conditions by the competent authority:

1. Member States shall take the necessary measures to ensure that competent authorities periodically reconsider and, where necessary, update permit conditions.
2. The reconsideration shall be undertaken in any event where:
   - the pollution caused by the installation is of such significance that the existing emission limiting values of the permit need to be revised or new such values need to be included in the permit,
   - substantial changes in the best available techniques make it possible to reduce emissions significantly without imposing excessive costs,
   - the operational safety of the process or activity requires other techniques to be used,
   - new provisions of Community or national legislation so dictate.

Article 18 - Community emission limiting values:

1. Acting on a proposal from the Commission, the Council will set emission limiting values, in accordance with the procedures laid down in the Treaty, for the categories of installations listed in Annex I except for the landfills covered by categories 5.1 and 5.4 of that Annex; and the polluting substances referred to in Annex III, for which the need for Community action has been identified, on the basis, in particular, of the exchange of information provided for in Article 16.
2. In the absence of Community emission limiting values defined pursuant to this Directive, the relevant emission limiting values contained in the Directives referred to in Annex II and in other Community legislation shall be applied as minimum emission limiting values pursuant to this Directive for the installations listed in Annex I.

Without prejudice to the requirements of this Directive, the technical requirement applicable for the landfills covered by categories 5.1 and 5.4 of Annex I, shall be fixed by the Council, acting on a proposal by the Commission, in accordance with the procedures laid down in the Treaty.

II.3.6. State of progress of BREFs on July 30, 2005

TWG & Members list	Documents available (see key below table)	Background material	Additional Information
Pulp and Paper manufacture	BREF (12.01)	List	Yes
Iron and Steel production	BREF (12.01)	List	Yes
Cement and Lime production	BREF (12.01)	List	Yes
Cooling Systems	BREF (12.01)	List	Yes
Chlor-Alkali manufacture	BREF (12.01)	List	Yes
Ferrous Metal processing	BREF (12.01)	List	Yes
Non-Ferrous Metal processes	BREF (12.01)	List	Yes
Glass manufacture	BREF (12.01)	List	Yes
Tanning of hides and skins	BREF (02.03)	List	Yes
Textile processing	BREF (07.03)	List	Yes
Monitoring systems	BREF (07.03)	List	Yes
Refineries	BREF (02.03)	List	Yes
Large Volume Organic Chemicals	BREF (02.03)	List	Yes
Smitheries and Foundries	MR BREF (07.04)	List	
Intensive Livestock Farming	BREF (07.03)	List	Yes
Emissions from storage of bulk or dangerous materials	MR BREF (01.05)	List	
Common waste water and waste gas treatment and management systems in the chemical sector	BREF (02.03)	List	Yes
Economic and cross media issues under IPPC	MR BREF (05.05)	List	
Large Combustion Plant	MR BREF (05.05)	List	
Large Volume Inorganic Chemicals – Ammonia, Acids & Fertilisers	MR D2 (03.04)	List	
Large Volume Inorganic Chemicals - Solid & Others	MR D1 (08.04)	List	

TWG & Members list	Documents available (see key below table)		Background material	Additional Information
Slaughterhouses and Animal By-products	MR	BREF (11.03)	List	
Food, Drink and Milk processes	MR	D2 (05.03)	List	Yes
Ceramics	MR	D1 (10.04)	List	
Management of Tailings and Waste-Rock in Mining Activities	MR	BREF (07.04)	List	
Surface treatment of metals	MR	FD (05.05)	List	
Surface treatments using solvents	MR	D1 (05.04)	List	Yes
Waste Incineration	MR	FD (05.05)	List	
Waste Treatments [Previously Waste Recovery/Disposal activities]	MR	FD (05.05)	List	
Speciality inorganic chemicals	MR	D2 (05.05)	List	
Organic fine chemicals	MR	D2 (12.04)	List	
Polymers	MR	D2 (04.05)	List	
Energy Efficiency	2003		List	

Key to “Documents available”:

BREF (mm.yy)	indicates that a document has been formally adopted by the Commission and can be downloaded by following the link which leads to the list of mirrors available and selecting the site nearer to you.
BREF (mm.yy)	indicates that a document has been finalised after submission to DG Environment and the final version dated as shown can be downloaded by following the link which leads to the list of mirrors available and selecting the site nearer to you.
FD (mm.yy)	indicates that a **Final Draft** document dated as shown has been put up for discussion with DG Environment and the Information Exchange Forum and the draft can be downloaded by following the link.
D1/2/3 (mm.yy)	indicates that a 1st / 2nd / 3rd working **Draft** reference document dated as shown has been put to consultation in the TWG and the draft can be downloaded by following the link.
MR (mm.yy)	indicates work has started, theTWG has met for the first time on date shown and a **Meeting Report** of that first meeting can be downloaded by following the link where shown.
yyyy	indicates work is planned to commence in the year shown and has not yet started.

The four ILE clusters have achieved their BREF, the last one being Surface Treatments.

II.3.7. Consequences for companies

The completion of BREF indicates the true start of the application of the Directive.

As with any European Directive, the IPPC is applied to every Member country and represents the minimum of what each of the existing and future Member States should apply to industrial installations covered by Appendix 1 of the Directive.

Currently one can assert that BATS contained in the various BREF will serve as a benchmark model but that in any case such BATS will not be made compulsory in industrial installations where these have limiting values of emission lower than those achievable by the application of BATS.

On the other hand, every Member country will be able to "make more severe" the Directive if it is considered useful in specific cases foreseen in the Directive. Thus Article 10 foresees that if a standard of environmental quality requires conditions more severe than those able to be achieved by the installation of BATS, supplementary conditions will be able to be required. The most typical example is that of installations close to ground-waters which will be able to be forced to operate under «zero waste» conditions.

Even in certain classical cases Member States already go further than the Directive by making IPPC compulsory for all companies of the same profession whatever their «size» whereas the Directive foresees application above a certain "size" of company that is defined in every BREF.

II.4. THE DIRECTIVE AND 'ILE'

Article 11 - 'Development in best available techniques' recognises that in time evolution of techniques will occur and that the Member States shall ensure that the proper authorities shall be kept informed of such developments.

In addition Annexe IV gives a list of factors to be considered during the evaluation of best available techniques; this list contains 12 points of which the first three are:

- use of low-waste technology,
- use of less dangerous substances,
- development of techniques for recovery and recycling of substances emitted, used in the process, and waste as appropriate.

The technologies evaluated and recommended in ILE fulfill, among others, these three criteria and thus make ILE an invaluable partner in the evaluation of the current BATS as well as in the assessment and development of emergent technologies.

Section 2

Waste-water Treatment Technologies Applicable to the Industrial Sectors in the ILE Network

CONTENTS

I.

INDUSTRIAL LIQUID EFFLUENTS IN THE PULP AND PAPER INDUSTRY

Cluster Leader

Technical Research Centre of Finland VTT, Finland - A. Mahiout.

Members

Enviplan Ingenieurgesellshaft (ENVIPLAN), Lichtenau-Henglarn, Germany - R. Damann.

Insititut National des Sciences Appliquées de Lyon (INSA), Villeurbanne, France - J. Pera.

Pirkanmaa Regional Environment Center (PREC), Finland - A. Luonsi.

Technical Research Centre of Finland VTT, Finland - M. Kolari, J. Siivinen.

Universidade Nova de Lisboa, Faculdate de Ciências e Tecnologiia, Portugal - J. F. Santos Oliveira, N. Lapa.

Université Montpellier 2, Institut Européen des Membranes (IEM-UM 2), France - G. Pourcelly.

Verein zur Förderung des Technologietransferts an der Hochschule Bremerhaven, Germany - F. Aslan.

INDEX

I.1. INTRODUCTION

Water is one of the basic elements for life on earth having many functions. Running water erodes soil and rock transporting the suspended, colloidal, and dissolved materials sometimes thousands of kilometres before being redeposited. Human actions are integrated into this circulation of material in natural water systems causing increasing pollution. Different methods of treatment are used to lower the pollutant load discharged to recipients. In nature, water purification takes a long time. Man-made treatment processes imitate the natural processes, but with accelerated speed. Such treatment processes include mechanical, physical, chemical, or biological processes either separately or in combination. Sewage purification includes both transformation and separation processes. In the transformation stage, dissolved and/or colloidal substances are converted by microbiological processes or by the addition of chemicals to form suspended particles. These suspended substances may then be removed from the water by sedimentation, filtration, or flotation. Acceleration of these processes needs energy to introduce oxygen into the water, to mix, transport, collect, and lift. Using such accelerated technologies residence times for treatment are below 12 hours. However the most common treatment methods by themselves are insufficient because a huge amount of money is necessary.

Production Integrated Environmental Protection (PIUS or Cleaner Production) could be a solution to enable a sufficient level of treatment to be reached. Cleaner Production increases the competitiveness of companies, leads to cost reductions, efficient use of raw materials and energy, and contributes to the optimisation of operative processes. The follow up, *Environmental Protection*, has also led to improvements in environmental protection standards with however, the disadvantage of considerable additional costs. PIUS follows a different strategy which is already being partly applied in some businesses.

PIUS is focused on: lower consumption of resources, lower consumption of energy and water, reduced waste, and waste-water containing fewer emissions, the strategy is fit for the future and is capable of producing more cost efficiency and using the available saving potential optimally. This is why PIUS features in both economic and ecological management.

Some applications of PIUS include:

- substitution of environmentally unfriendly auxiliary and industrial materials,
- application of efficient and innovative processes,
- use of energy saving systems, i.e. heating,
- management of the internal circulation of used materials,
- valuable utilisation of unavoidable residues,
- awareness of pre- and post-production processes,

- development of ecologically-friendly products (e.g. longevity, ease of repair, lower energy consumption, ease of recycling, etc.),
- use of, as opposed to, sale of products (i.e. ecology leasing).

Currently production integrated environmental protection is one of the key topics in the pulp & paper industry. This guide-book on best available techniques (BAT) in the pulp and paper industry reflects the information exchange carried by different European experts. This guide-book gives a general overview on processes in the pulp and paper industry, its typical effluents, and available techniques of treatment, especially water. In terms of an efficient environmental protection strategy right from the design or planning stage this guide book should be considered very seriously. It is also very essential in process design and should also be observed more carefully for future technical solutions.

This guide-book is an addition to the Reference Document on best available techniques in the pulp and paper industry which reflects the results from an exchange of information according to Article 16(2) of Council Directive 96/61/EC. The Best Available Techniques Reference Documents (in short: BREFs) are published by the IPPC bureau (IPPC = Integrated Pollution Prevention and Control) in Sevilla (Spain):

“Paper is essentially a sheet of fibres with a number of added chemicals that affect the properties and quality of the sheet. Besides fibres and chemicals, manufacturing of pulp and paper requires a large amount of process water and energy in the form of steam and electric power. Consequently, the main environmental issues associated with pulp and paper production are emissions to water, emissions to air, and energy consumption. Waste is expected to become a gradually increasing environmental issue of concern.”

On 23 October 2000, the “Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy” or in short the EU Water Framework Directive (or even shorter the WFD) was finally adopted. This Directive is the most substantial piece of water legislation from the EC to date. It requires all inland and coastal water bodies to reach at least “good status” by 2015. It will do this by establishing a river basin district structure within which demanding environmental objectives will be set, including ecological targets for surface waters. The Directive therefore sets a framework which should provide substantial benefits for the long term sustainable management of water. The implementation of Water Framework Directive has started in most of the EU countries and it will have a strong affect on which discharges/impurities will be important to limit in the future, how effluents are measured, and which water systems are controlled. This guide-book should help to realise water treatment processes in accordance with the requirements of WFD.

This guide-book covers the relevant environmental aspects, especially concerning water treatment aspects, of pulp and papermaking. Neither environmentally relevant upstream processes like forestry management, production of process chemicals off-site, and transport of raw materials to the mill nor downstream activities like paper converting or printing are included in this document. Environmental aspects which do not specifically relate to pulp and paper production such as storage and handling of chemicals, occupational safety and hazard risk, heat and power plants, cooling and vacuum systems and raw water treatment are not considered.

This guide-book should help to achieve economical and ecological goals simultaneously.

I.2. TREATMENT PROBLEMS (ORIGIN AND COMPOSITION)

The paper and pulp industry produces a wide range of goods that are used for packaging, communications, printing, and for sanitary and household purposes. Paper is made from wood and non-wood fibres and requires huge amounts of water and energy in its production. The admission of Austria, Finland, and Sweden to the European Union (EU) in 1995 considerably affected the structure and the importance of the EU Forest Based and related Industries (FB-IND) which is now one of the largest industrial sectors in the EU. Thus, the European pulp production has tripled, paper and board production increased by 50%, mechanical woodworking output increased by 30% and the printing and publishing industries expanded by 10 - 15%.[1] The waste-water produced during paper and board manufacture contains pollutants which can be removed by appropriate cleaning processes.

In 1998, according to EU statistics (Table 2.1), the EU Forest Based and Related Industries (FB-IND), accounted for a total of around 63,000 companies, ranging from a considerable number of SMEs to a small number of large global corporations. The biggest companies of the EU/FB-IND are to be found in the pulp, paper and board, and publishing sectors in which there is the greatest concentration of activity. In these sectors, the 20 largest companies account for 60% of the total turnover.[1]

	Production value M €	%	Value added at factory cost M €	Number of Enterprises (1995)	Number of persons employed
Mechanical woodworking excluding furniture	60,158.6	19	18,760.7	29,113	526,679
Pulp, paper and board manufacturing	55,223.5	17	16,066.2	930	217,175
Paper and board converting	55,738.4	18	18,070.0	5,009	381,582
Printing	61,184.1	19	26,429.8	20,606	626,098
Publishing	86,362.4	27	32,258.6	7,488	627,409
Total FB-IND	**318,667.0**	**100**	**111,585.3**	**63,146**	**2,378,943**

Table 2.1. Forest-based and related industries in the EU 1998; Source Eurostat (Enterprises with less than 20 employees are not included

According to the data of the Confederation of European Paper Industries (CEPI), the total production of paper and paperboard in Europe was more than 90 Mt in year 2000 (Figure 2.1). Graphic paper grades make up around 50% of the EU paper production, packaging paper grades account for 40%, and hygiene and specialty papers around 10%. Germany leads the field as the largest paper producer in the EU, followed by Finland, Sweden, and France. Finland and Sweden are the main pulp-producing countries.

OECD countries account for around 76% of global paper consumption measured in tonnes, but the demand in OECD countries is oriented towards strong, glossy, and sophisticated paper products, so the value of the OECD countries share in total paper consumption is somewhat higher.[3]

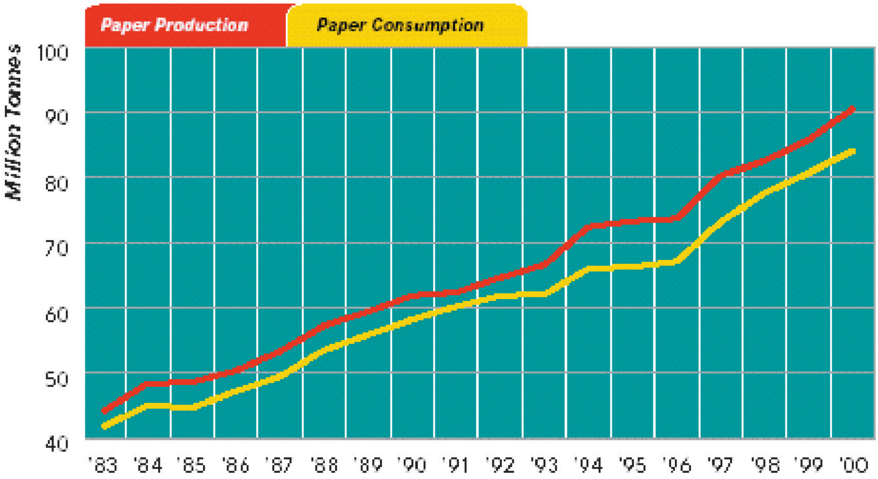


Figure 2.1. Paper Production and Consumption in CEPI 1983-2000 (Source: CEPI)

Pulp and paper production is associated with increased deforestation, water contamination, air pollution, and the release of greenhouse gases. Water is used both as a suspension and transport agent for fibres and fillers, as a solvent for chemical additives, and as a medium promoting hydrogen bonding between the fibres. Figure 2.2, shows a simple flow chart of paper production with the main focus on water management.

Practically all papers and boards are produced on continuously (or in the case of boards sometimes semi-continuously) operating machines, the principle of which is the dewatering of the aqueous fibre suspension on a wire to form a fibrous mat which is then pressed and dried. The sheet of paper thus produced is packed in the form of rolls or packs of sheets. The pulp fibres are pre-treated to give them the properties required for the individual type of paper. During the process of paper production, kaolin, $CaCO_3$, talc, and/or TiO_2 are added to the pulp, to give the paper a whiter colour. Also chemicals such as organic fillers (starch, latex), colours, aluminium sulfate, etc. are used to make paper with different properties or to simplify the process. Paper can be decoloured, which can be done by either, washing the pulp with a large amount of water or washing with a small amount of water plus additions like sodium silicate, sodium carbonate, fatty acids, or non-ionic detergents.

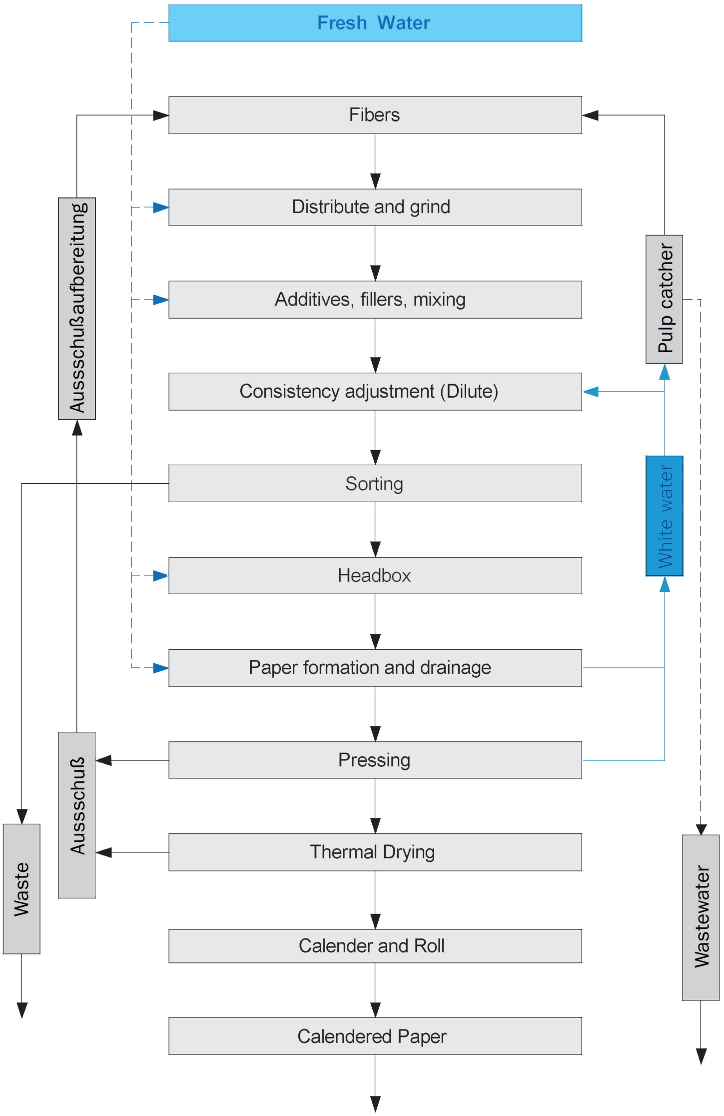


Figure 2.2. Flow chart of paper production[4]

Water is an important consumable in the production of pulp and paper, is required in relatively large quantities and must meet certain minimum purity criteria. It must be processed, but can be recycled in internal circuits a number of times.

Water usage and the amounts of waste-water are characterised by a specific value which is related to the volume produced. These values can be influenced by the different rates of internal water re-circulation. The quantity of waste-water is approximately the same as the quantity of fresh water used. Thus a reduction in fresh water consumption by creating internal circuits results in a reduction of the quantity of waste-water produced, which is also a major cost factor when designing waste-water treatment plants. According to OECD, in 1995 the pulp and paper sector was responsible for around 11% of the total volume of water used in industrial activities in OECD countries. Reference scenario projections indicate that world-wide water use by the sector is likely to grow from 11 to 18 billion m^3 between 1995 and 2020.[3] The results of the specific amounts of waste-water since 1974 in Germany are illustrated in Figure 2.3.[4] Over the years there has been a progressive reduction in the use of water at mills considered in relation to all types of mills. Thus average water consumption in paper production has decreased in Germany from 46 to 13 L/kg during the years 1974-1996.[5] Even so, water consumption levels are still high and in the future it will be desirable to achieve further reductions, as paper production is increasing, which is in turn an important indicator of a country's economic situation. The consumption of water depends on the production of different sorts of paper and production processes. Table 2.2 lists the volume of waste-water and the concentration of the important parameters BOD_5, COD, and AOX for some types of paper.

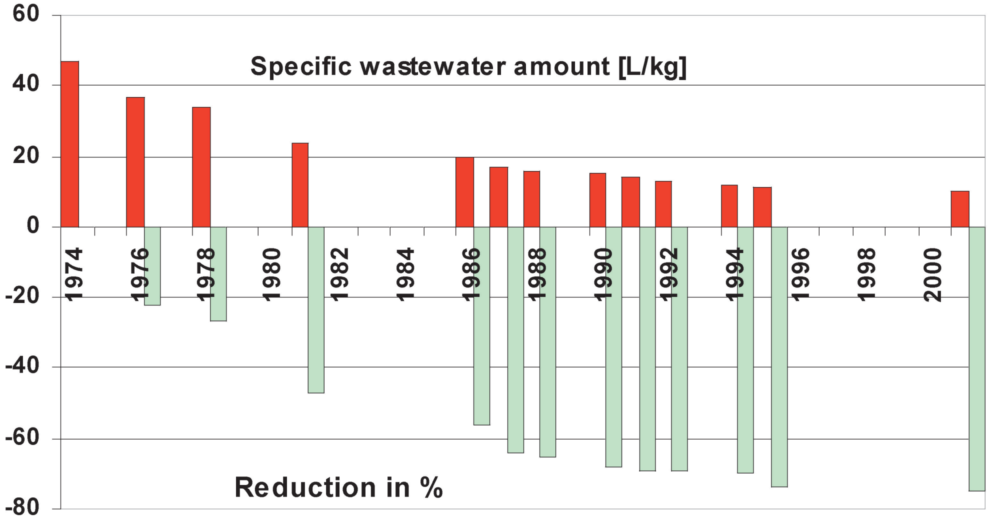


Figure 2.3. Specific waste-water amounts and reduction in Germany[4]

Product group	Concentration [mg/L]			Specific waste-water volume [L/kg]
	BOD_5	COD	AOX	
wood containing[1)] paper	10-550	20-1100	0.05-6	5-250
wood free[2)] paper	125-500	320-1300	0.03-0.35	8-30
recovered paper	250-3000	540-5680	0.1-2	0-20

1) containing not only pure, chemically produced pulp but also ground wood, chemical-mechanical pulp, etc.
2) containing only chemically produced material.

Table 2.2. Typical ranges of the concentrations and the specific waste-water volumes for some types of paper[4]

References for Part 2

1. The state of the competitiveness of the EU Forest-Based and Related Industries, Draft Communication to the Council, the European Parliament, the Economic and Social Committee, and the Committee of the Regions, 04.10.99
2. http://ec.europa.eu/enterprise/forest_based/pulp_en.html#2
3. OECD – Environmental Outlook, 16 May 2002, (www.oecd.org)
4. C. H. Möbius: Abwasser der Papier- und Zellstoff-industrie, 3. Auflage, Augsburg November 2002 (www.cm-consult.de)

I.3. OPTIMUM AND HIGH EFFICIENCY WASTE-WATER TREATMENT TECHNIQUES IN THE PULP AND PAPER INDUSTRY

I.3.1. Removal and transformation requirements for pulp and paper mill effluents

Pulp and paper mill effluents contain following major groups of constituents and compounds:

- wood in its original state or transformed by mechanical and chemical treatments,
- chemicals in their original or transformed state,
- used additives like fillers, complex formers, and optical brightening agents,
- other undefined constituents and compounds.

Pulp and paper mill effluents often have typical characteristics like:

- fairly high temperature and pH far from neutral,
- high variation of concentrations and loading of pollutants,
- low content of nutrients (P/N) in respect to organic matter and thus to bacterial growth.

Therefore, in the treatment of pulp and paper mill effluents as one part of the mill operation the following aspects need to be considered:

- equalization of load,
- control and adjustment of pH and temperature,
- addition of nutrients.

The requirements listed above naturally depend on the type of treatment processes used.

The need to remove disturbing agents e.g. from the circulation water of a wood containing paper producing mill depends on the specific water consumption (SWC) as follows:

- removal of suspended solids when the SWC is 8-10 m^3/t,
- removal of dissolved organic matter when SWC is 4-8 m^3/t,
- removal of inorganic matter when SWC is 2-4 m^3/t.

Development towards closed water systems in paper-making is proceeding steadily with for example successful mill examples from the medium level of the above categorization.[1] However, the easy, initial phase in closing water circuits seem to be over at least for bleached Kraft production.[2] Lately the trend has been to aim at a more moderate recycle and recovery of bleach plant filtrates than was the case 5-10 years ago, because of problems with scaling, deposits, chemical consumption, pulp quality, etc.. The same applies for both "ECF and TCF" Kraft pulp mills. If the goal was 0-10 m^3/ADt of effluent from the bleach plants 5-10 years ago, the goal today, at least in Sweden, is rather (10) 15-20 m^3/ADt of effluent from the bleach plant.[2] Therefore, dramatic changes are unlikely to affect the perspective of the needs for waste-water treatment.

Methods commonly used for removal of suspended solids are settling, filtration, and chemical precipitation. Removal of organic matter within the production processes is usually achieved using membrane filtration and chemical precipitation. Removal of inorganic matter requires evaporation or reverse osmosis. For successful operation, all of these methods demand a certain level of waste-water quantity and quality equalization. Requirements for equalization and adjustment of parameters tend to increase when using external biological waste-water treatment processes. Adjustment of pH and temperature is necessary for bioprocesses as well as equalization of load and addition of the required amount of nutrients.

When the transition to more sophisticated external waste-water treatment systems has started in Northern Europe, one of the measures has been to construct a system to hinder temporary overflows. These include systems to collect and return black liquor and fibre spills. Also special emergency basins were built for waste-waters formed under exceptional operating situations.

Control of pH applies to most of the processes used. Temperature control is important in production processes and in biological waste-water treatment. Basins to equalize loading in mills using mechanical-biological effluent treatment, have normally been constructed between the primary clarifier and the biological unit. In these basins a slight amount of biological activity already takes place. Depending on the bioprocesses used, the addition of nutrients has to be focused at points prior the actual nutrient uptake by the micro-organisms.

I.3.2. Equalization

Recently, as the operation of waste-water treatment plant has improved considerably, the importance in this development of the equalization of loading has continuously increased. This activity can be classified according to the place where it is implemented. Within the mill, monitoring and equalization thereafter can be made. In the treatment plant, construction of equalizing basins is the major option.

Within the mill, measurements are preferably implemented by departments or process sections using automatic sampling as well as on-line pH, conductivity and suspended solids measurements. Such monitoring can be connected to recovery systems for black liquor and fibres. Successful operation requires relatively quick reporting system in the mill. Improvements can easily be made in most of the mills in this respect.

Equalizing basins in waste-water treatment plants have normally been constructed after the primary clarification and cooling and before the aeration basin if an activated sludge process is the method of treatment. In the design of an equalization basin both the variation of quality and quantity is taken into account. The usual target is that the hourly COD-loading should not alter more than 15-20%. Well operating basins have been 3-4 m deep, equipped with surface aerators or mixers with a hydraulic retention time of 8-10 h. In these basins a BOD-reduction of 10-20% is normal and accordingly some biosludge is formed. High BOD-removal is not advisable because the sludge formed affects the settling characteristics of the resulting activated sludge. Overall equalization contributes to better treatment results and reduced adjustment requirements in the subsequent stages of treatment.

Emergency basins have also been constructed in treatment plants and any spills are conducted to them preferably after primary sedimentation. Emergency basins provide storage from which pumping to the treatment process starts during their filling. One of the major problems in efficient emergency basin use is the transfer of information in real time. For example, often information of discharges of high dissolved matter is received only after sampling and laboratory analyses, say 12-24 h after the start of this phenomenon. To be effective, on-line measurements like COD or suspended solids is necessary; otherwise the use of these emergency basins remains only for those exceptional discharges which are known in advance, such as the service and maintenance of process basins. To be useful the capacity of emergency basins should be designed for 12-24 h waste-water discharge. Suspended solids removal has to be introduced either by primary clarification or by temporary dredging.

I.3.3. Control of pH and temperature

A prerequisite of a successful operation of biological waste-water treatment processes is a proper pH control system. The appropriate pH-range for an activated sludge process operation is 7.0-7.5. To achieve this with pulp and paper mill waste-waters, the influent pH has to be adjusted to 6.5-8. After this, the pH will be regulated through the production of carbon dioxide from biological degradation as well as through other changes in the waste-water composition. Organic acids will usually be degraded quickly by the micro-organisms. Control of pH may also be necessary to reduce the potential for corrosion or for optimizing conditions for chemical precipitation.

Adjustment of pH is usually implemented before primary sedimentation as change in pH usually leads to precipitation of dissolved organic compounds. The appropriate way to remove these precipitates is to combine it with fibre removal. For both technical and economical reasons sulfuric acid and calcium oxide or calcium hydroxide are most commonly used chemicals for pH adjustment. The slow dissolution (5-10 min.) and reaction time (10-20 min.) of the calcium based chemicals challenges the configuration of the reaction basin and mixing and measurement requirements.

The temperature target for the most commonly used processes like activated sludge are between 20°C and 38-40°C. Organic matter removal including biosludge decomposition increases with increasing temperature. Also the diversity of microbial species is said to be highest at temperatures below 40°C and this improves the potential for degrading the waste. Dissolution of oxygen, however, decreases with increasing temperature.

Cooling of the waste-water can be implemented either partly or completely by the indirect use of heat exchangers. However, the possibilities of using "hot" water with a relatively low temperature in the mill are very limited. Cooling towers are used for direct waste-water cooling with air. These are located in the process configuration so that problems from suspended solids are minimized. Thus an appropriate location would be after primary sedimentation and before the regulation basin.

I.3.4. Suspended solids removal

Suspended solids like sand, coarse wood particles, fibres, as well as additives and fillers used in papermaking are typical targets for removal in pulp and paper mill waste-waters. Particles with high specific weight are usually removed by sedimentation. Within the mill processes sorters are also used. The separated sand is conducted out of the process with the rejects.

In specific cases sand removal has also been installed for mill canalization and as the first step in the external waste-water treatment plant. Usually these sand removal units are designed to remove particles coarser than 0.3 mm diameter. Design principles are the same as those used for municipal waste-water treatment plants.[3]

Coarse particles are removed with screens. A coarse screen with 50-80 mm openings is installed as a first step, followed by a fine screen with openings of 15-30 mm. In specific cases, even finer screens or drum filters are used. Screens are usually equipped with hydraulic cleaning devices operated through water level control. Overflow arrangements for clogging situations are normally included. The waste from these screens is mainly wood and is usually incinerated.

Removal of suspended solids from pulp and paper mill waste-waters has been achieved with many different kind of methods and equipment, for example:

- different kinds of belt filter,
- sedimentation basins,
- flotation units,
- membrane processes, mainly ultra-filtration.

Different kinds of belt filters are normally found in the range of equipment in pulp and paper mills. Their design and use has been described in both appropriate text and hand-books covering the field.[4] Sedimentation basins or clarifiers are used to remove suspended solids before other waste-water treatment processes. They are also used as secondary clarifiers after biological reactors such as the aeration basin in the activated sludge process. Basic information and design principles are easily found in the literature.[4] For waste-waters from the forestry industry as well as for specific waste-waters in general, basic measurements such as settling velocity and sludge characteristics have proved very useful as a basis for the design. In the design of primary and secondary sedimentation basins for waste-waters from the forestry industry, following parameters are typical (Table 3.1):

	Primary Clarifier	Secondary Clarifier (for activated sludge process)
Surface loading, m^3/m^2h	0.8	0.5-0.6
Hydraulic retention time, h	4-5	4-6
Peripheral loading, m^3/mh	4-6	3-5
Sludge consistency, %	3-5	0.6-0.8
Effluent SS, mg/L	40-80	10-30

Table 3.1. Basic Design of Sedimentation Basins

In primary sedimentation, traditional scrapers are normally used for sludge collection and removal. For operational safety, and for improvement of the results of treatment, on-line consistency and sludge surface indicators have been installed. Scrapers with sludge suction have been widely introduced since late 1980s in the secondary clarifiers of activated sludge plants. A major reason for this introduction was to reduce phosphorus release from the settled sludge by quick removal of the sludge. This reasoning has partly been proven to be due to unreliable results of measurement. Also the low adjustability of sludge recycling rate and the tendency to clog have eroded the usefulness of this technique. Thus the demand for traditional scrapers will stay. Surface sludge removal with surface scrapers has not proven to be beneficial. In activated sludge plants both theoretically and in practice relatively deep (4-5 m) and high volume (≥ 25 % of aeration volume) secondary clarifiers have proven successful. Flotation has a long tradition in pulp and paper industry processes. Design and operational information is widely available.[5] Currently flotation equipment serves mainly as a pre-treatment for waste-waters but also as a tertiary treatment after biological processes with or without the addition of chemicals. Fairly usual improvement requirements for the operation of chemically aided flotation have been the following:

- assurance of flock formation of suspended solids in the waste-water,
- assurance of quantity and quality of dispersion water,
- assurance of proper nozzle operation,
- guarantee of sufficient hydraulic retention time within the flotation basin.

It has often been found that flotation equipment suitable for fibre removal in the primary stage is not directly applicable to biosludge separation or in operations involving chemical treatment.

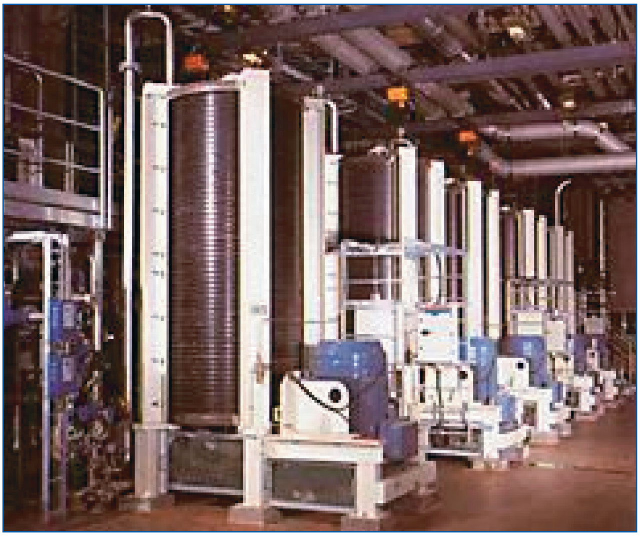


Figure 3.1. Cross-flow membrane unit installation in a paper mill[6]

Membrane processes were introduced into pulp and paper mill waste-water treatment with the start of the treatment of bleaching effluent. Previously, reverse osmosis had been used for specific purposes like water for steam generation. Currently membrane applications, mainly ultra-filtration, can be found in paper mills e.g. for coating colour recovery and also for purification of circulation waters.*

Removal of extractives, particularly resin agglomerates, fine suspended matter and other compounds of colloidal nature has been successful with ultra-filtration membranes. As noted earlier, this is the case when specific fresh water consumption is in the range of 4-8 m^3/t of wood containing paper. Also nano-filtration has been tested. The design of the equipment depends on the type of frame equipment and naturally on the characteristics of the membranes.[7] Reverse osmosis has been tested and proposed for removal of dissolved inorganic matter but in the pulp and paper industry there have been very few applications outside water production for power plants. The most recent interest in the application of membranes is for the separation of sludge in biological treatment processes. Tertiary treatment with membranes after biological treatment has been successful at least at the scales used in different research projects. This guarantee of the level of quality is necessary, especially if the treated water is to be reused. It seems that membrane processes have plenty of potential application for pulp and paper industry waste-waters and obviously membrane processes will increasingly be applied for the treatment of circulation waters.

---

* See Section 3 – Membrane Processes, for further information.

I.3.5. Organic matter removal with biological processes

For the removal of organic matter from pulp and paper mill waste-waters the following main processes have been used:

- aerated lagoon,
- activated sludge process,
- bio-filter,
- combination of anaerobic and aerobic processes.

Before applying these processes, the waste-water pH has to be adjusted and generally regulation of loading is useful.

Aerated lagoons have been constructed when geographical and other natural conditions have been favorable. Due to their limited controllability, the results achieved have been diverse.

The design of successful applications[3] has included the following features:

- volumetric loading 60-80 g BOD/m^3d,
- hydraulic retention time 4-6 days,
- minimum mixing capacity 4-6 W/m^3,
- oxygen requirement of the order of 1-1.2 kg O_2/kg $BOD_{removed}$

A length/width ratio of 4 or more is usual in the aeration basin. The first third of the aeration basin requires half of the aeration capacity. As a result, mixing efficiency is limited at the end of the basins. Modeling of mixing conditions has proven useful in the design process. BOD can be removed with aerated lagoons down to 10-30 mg/L. Suspended solids, including those from growth of biomass can only be removed up to 30-50%. For more effective separation chemical precipitation and flotation can be used. With these processes, appropriately installed, purification results can approach those of a well operated activated sludge process.

The activated sludge process in its present form (Figure 3.2) is the most widely used method in countries having an extensive forestry industry. A well operated activated sludge process for pulp and paper making waste-waters includes the following features:

- sludge loading is of the order of 0.2 kg BOD/(kg sludge*d),
- aeration basin includes 3-4 aerobic selectors[8],
- sludge age 10-25 days,
- the ratio of aeration volume and secondary settling volume 4:1.

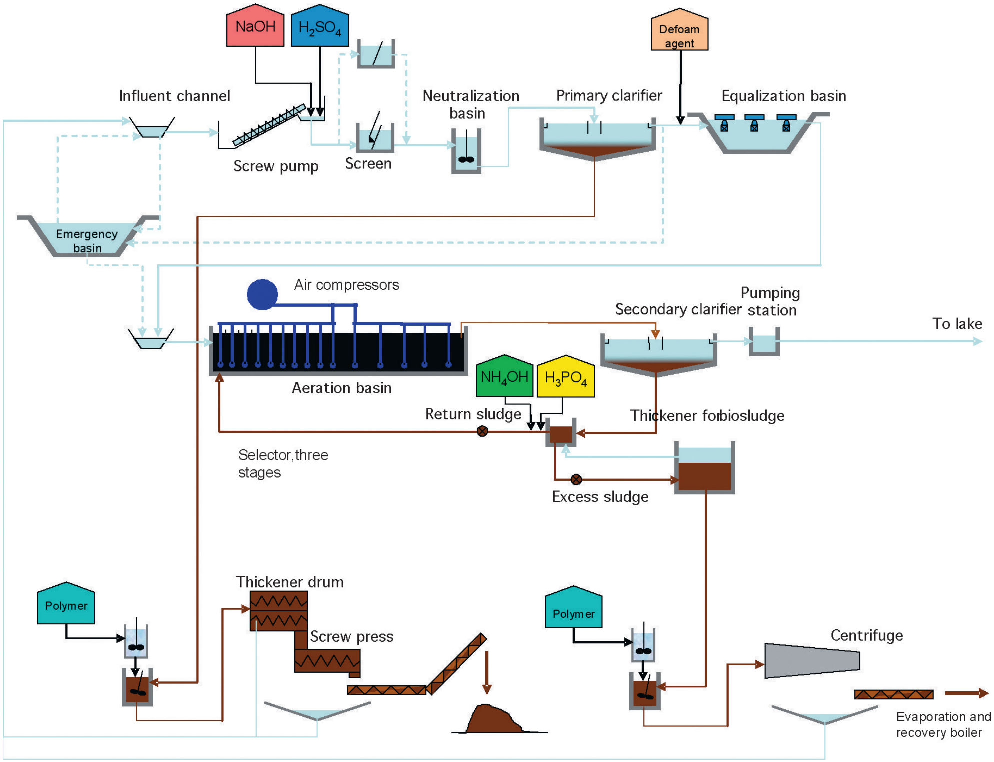


Figure 3.2. Typical activated sludge plant for a pulp mill

Additionally, the following features bring techno-economical benefits:

- plant with only one aeration tank and aerators that can easily be raised,
- nutrients that are preferably added in fluid form to the recycled sludge,
- pumping capacity of recycling sludge such that the “flock load” does not exceed 0.25-0.3 kg COD/(kg return sludge).

The treated effluent of a well controlled and operated activated sludge plant is typically:

- suspended solids 10-30 mg/L,
- dissolved BOD 0-10 mg/L,
- dissolved phosphorus 0.1-0.2 mg P/L and dissolved nitrogen 1.5-2 mg N/L.

Thus the final loading to the recipient from a properly designed and operated bioprocess is highly dependent on the escaping suspended matter. If the escaping mass is bio-sludge, 20-30 % of the mass can be estimated as the amount of BOD.

The advanced form of activated sludge plant, a membrane bioreactor, has been tested.[9,10] and also at elevated temperatures compared to the possibilities of conventional activated sludge process.[11] Full retention and control of biomass in the reactor opens interesting operational possibilities. After progress in the prevention of fouling, this configuration can improve both the level of purification as well as its uniformity and reliability which finally define the absolute reduction of loading to the receiver.

The most widely applied bio-filter is the fluidized bed reactor (Figure 3.3). The design of these plants is usually based on laboratory and pilot-scale experiments. The volume of the reactor, including the diverse carrier materials used, is defined by such experiments.

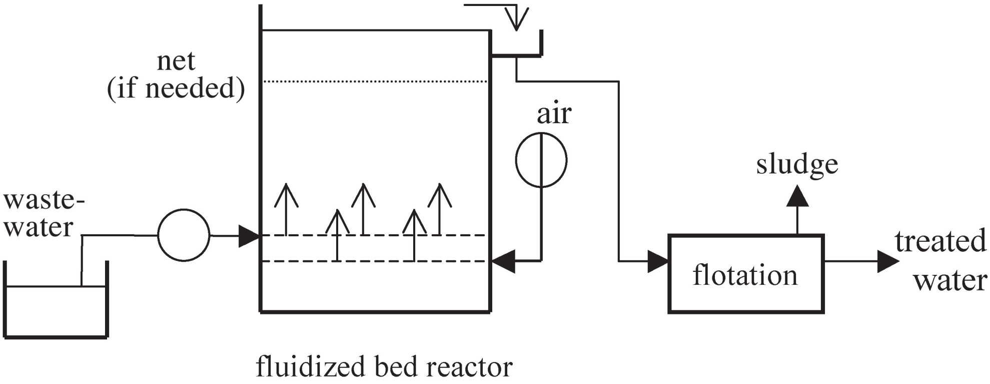


Figure 3.3. Diagram of a fluidized bed reactor

Most often the volumetric loading has been 7-10 kg COD/m^{3}d. The design of the plant has to include the requirement of oxygen and nutrients as well as an estimate for biomass production. The sludge produced is often separated by flotation. Before the reactor the minimum requirements are the control and adjustment of pH and temperature. Results for pulp and paper mill waste-waters are removal of 70-80% BOD and 40-60 % COD. These plants have most often been installed in cases where existing waste-water treatment capacity has been exceeded. The major advantage of this configuration is its relatively low area requirement.

	BOD_{5-7}			COD_{Cr}		
	Kraft[1]	WC[2]	WF[3]	Kraft	WC	WF
Activated sludge	95-99			50-70	70-90	80-90
Aerated lagoon	70-95	70-85		40-60	70-85	
Filters (fluidized bed)	70-80	70-85		40-60	50-70	

1) Kraft = elemental chlorine free bleached kraft production
2) WC = wood containing paper production
3) WF = wood free paper production

Table 3.2. Typical removal (%) of organic matter with well-designed and operated biological treatment methods (removal % with total effluent concentration)

Anaerobic treatment has been used as a pre-treatment for pulp and paper mill effluents in cases where the concentration of degradable organic matter in the effluent has been high, typically >1000 mg COD_{Cr}/L. Suspended solids concentration to and also from the anaerobic unit should be low.

The amenability of anaerobic process to cut the organic loading in such cases before aerobic treatment, compared to aerobic treatment alone, is based on the following advantages:

- reduced need for nutrients,
- reduced energy consumption,
- reduced sludge production,
- stabilization of operation when reducing the excess loading before aerobic treatment,
- energy production.

An example of the possible arrangement of a treatment system utilizing an anaerobic process is shown in Figure 3.4.

The majority of applications of such systems are in paper mills, often using waste-paper as raw material and increased water recirculation. The up-flow anaerobic sludge blanket (UASB) reactor has just recently been superceded by the internal circulation (IC) reactor as the most commonly used type of reactor. Both of these reactors include acidogenic and methanogenic phases as well as the separation of solids at the top. For the design, measurements of the actual characteristics of the target waste-water with laboratory and pilot-scale studies are advisable. For pulp and paper mill effluents a safe range of COD loading for good operation has traditionally been 5-8 kg COD/m^3d, although considerably higher values have been given by the manufacturers of for example IC-reactors. A surface loading less than 1 m/h is advisable in UASB reactors. Reductions of 50-60 % COD and 70-80% BOD can be expected. Specific attention has to be paid to suspended solids, sulfur, extractives, volatile fatty acids and alkalinity.

Sulfur containing waste-waters need specific process development and operational configurations.[12] Aerobic treatment after the anaerobic stage and also after other types of aerobic pre-treatments can be designed normally, if solids separation in the pre-treatment unit is properly implemented.

Final effluent quality after anaerobic-aerobic treatment, naturally depending on the diversity in waste-water characteristics, can reach <10 mgBOD/L and <100 mgCOD/L. Internal treatment and reuse (environmentally friendly) utilizing process configurations like the one given above are possible when low quality brown products are manufactured.[1]

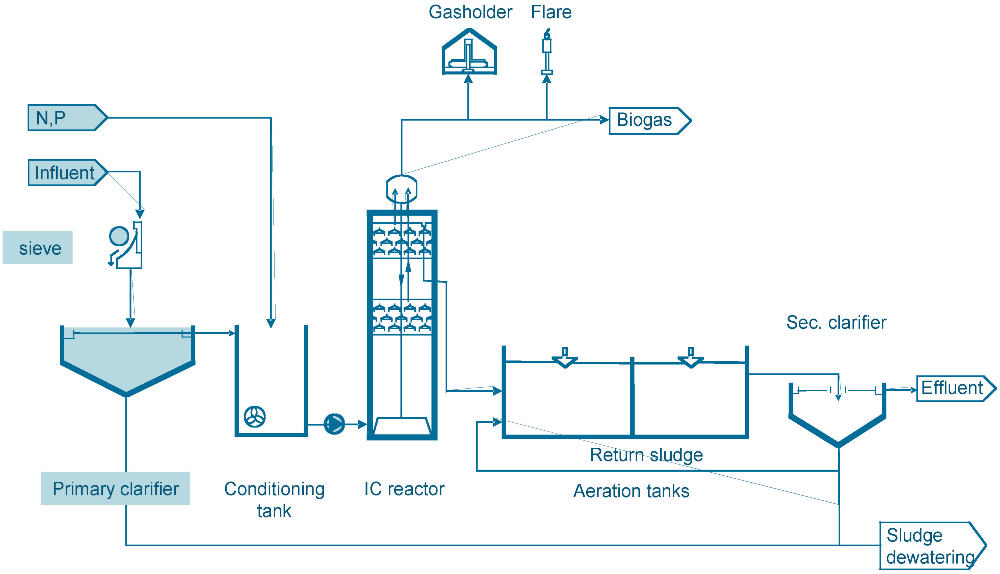


Figure 3.4. General flow diagram of a waste-water treatment system of a pulp and/or paper mill utilizing anaerobic pre-treatment of combined effluent with high degradable organic matter content[13]

Cost comparisons are often given from cases where anaerobic treatment unit has been added to the front of the existing overloaded aerobic treatment system. In a typical case of this kind, the equipment manufacturers can propose operational cost saving per ton of product to be double of that required for the investment of the additional anaerobic unit (20 years, 7% interest).[13] The payback time can be less than 10 years, which used to be appropriate according to traditional economic thinking, but may well be insufficient for the current extremely short term approach.

An example of a Portuguese mill complex (Plant A, certified according to ISO 9002) includes two industrial units that work in an integrated way. The mill producing bleached eucalyptus pulp sends almost 40% of its production to the printing and writing paper mill. In the pulp mill there are two effluent streams (Figure 3.5): an acidic one (produced during bleaching and demineralization) and an alkaline one (rich in TSS, produced from several process steps, such as boiling, washing, screening, bleaching, caustification, evaporation, lime ovens, boilers, turbines, demineralization, etc.). These two effluents are submitted to primary treatment (sedimentation and neutralization), followed by activated sludge treatment. In the paper mill there is only one effluent (produced during the pulp preparation, paper machinery and additives production). This effluent is first treated by a primary process followed by a Sequential Batch Reactor (SBR) process (Figure 3.6).

Table 3.3 shows the average characteristics of the crude waste-water from the pulp mill into the treatment system. The characteristics of the treated waste-water and treatment efficiencies are also shown. The average values obtained in the treated effluent of the pulp mill are below the legal emission limits. In this mill, the pulping technology used is an Elementary Chlorine Free (ECF) process. Therefore, the percentage removal of 40% is sufficient to meet the legal emission limit. The average characteristics of the paper mill waste-water and of the treated waste-water are shown in Tables 3.3 and 3.4.

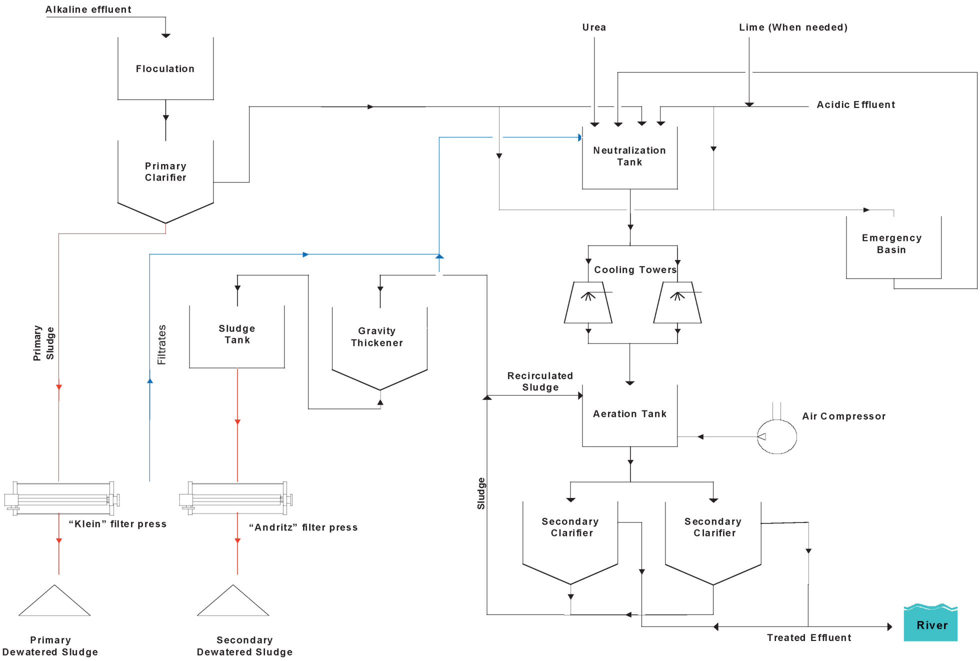


Figure 3.5. Flowsheet of the treatment plant of the waste-water pulp mill produced at Plant A (communication from the Plant A Administration, 2004)

Waste-water/Parameter	TSS	BOD_5	COD	AOX
Crude waste-water (mg/L)	180	260	1163	13
Treated waste-water (mg/L)	36	23	384	8
Treated waste-water (kg/tAD)	2.0	1.3	16.0	0.14
Treatment efficiency (%)	80	89	67	40
Emission limits to be achieved (kg/tAD)	3.0	6.0	50	1.5

Table 3.3. Chemical characteristics of waste-waters and treatment efficiencies for the waste-water treatment system of pulp mill (Plant A): average values for the year 2002 (communication of the Plant A Administration, 2004)

All the average values were below the legal emission limits for all chemical parameters. The removal efficiencies for TSS and BOD_5 were high. The removal efficiencies for COD and AOX were not so high as for TSS and BOD_5, nevertheless, they were high enough to meet the emission values.

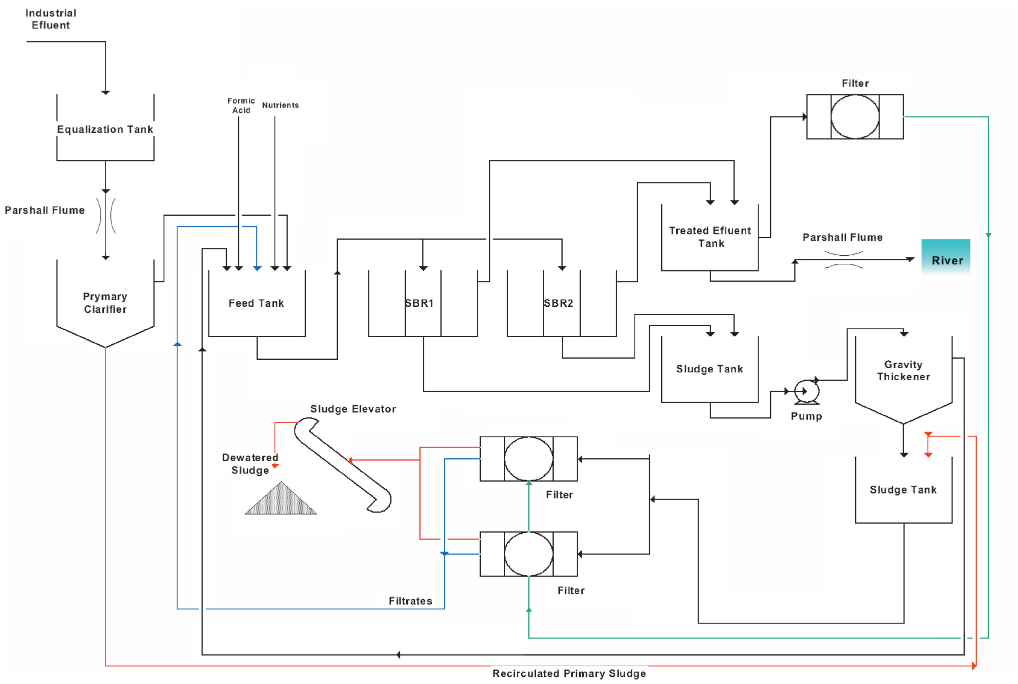


Figure 3.6. Flowsheet of the treatment plant of the waste-water paper mill produced at Plant A (communication of the Plant A Administration, 2004)

Waste-water/Parameter	TSS	BOD_5	COD
Crude waste-water (mg/L)	92	247	446
Treated waste-water (mg/L)	36	8	80
Treatment efficiency (%)	45	96	81
Emission limits to be achieved (mg/L)	60	40	150

Table 3.4. Chemical characteristics of waste-waters and treatment efficiencies for the waste-water treatment system of paper mill (Plant A): average values of the year 2002 (communication of the Plant A Administration, 2004)

The annual average costs of the operation for both waste-water treatment plants are shown in Table 3.5.

Treatment plant	Annual Costs (k€)
Waste-water treatment plant of pulp mill	1700
Waste-water treatment plant of paper mill	370

Table 3.5. Average annual costs of the operation of pulp and paper waste-water treatment plants (communication of the Plant A Administration, 2004)

I.3.6. Methods of removing inorganic matter

Removal of inorganic matter from waste-waters becomes necessary when re-use of water in the production process, i.e. recycling, increases. At mills manufacturing wood containing paper, the limit of specific water consumption has been observed to be 2-4 m^3/manufactured ton. The need is naturally specified according to the required properties of the water to be used. The techniques employed have so far included the following[†]:

- evaporation with various types of equipment,
- reverse osmosis (membrane technique),
- freezing.

For evaporation plenty of suitable technology have been developed.[5] Most equipment applied to forest industry waste-waters has also been used for other purposes. One of these has been the removal of salt from seawater to produce process water. Several dozen examples of the use for pulp and paper industry waste-waters of evaporators built for different purposes and built in

---

[†] See also Evaporation and Membranes – Section 3.

slightly different ways are known. Most of them are components in systems that also include other methods. In addition to removing inorganic matter, evaporation also removes other waste matter from the forest industry waste-waters. The concentrates that result from evaporation of waste-waters provide special problems. Also investment and operating costs are currently markedly high. There are still some technical problems depending on the application but they are being gradually solved. The best techno-economic solutions have usually been found in integrated operations in which evaporators are also used for other purposes.

Reverse osmosis has been tested and developed over a long time. The amount of equipment in use is large although it has not been extensively used within the forest industry.[7] The reasons for this have been techno-economic and include the fate of the concentrates. Motives for the application for reverse osmosis and for other membrane techniques have resulted from the vision of zero-emission mills[14] and as part of a total solution they have included together with other waste-water treatment techniques.

Freezing has been tested and used as part of waste-water treatment. In the forest industry such experiments have mainly been made in Canada. The use has not been particularly extensive. The problems still seem to be in the application of the technique.

I.3.7. Combination of different methods of treatment

At pulp and paper mills, waste-waters are currently treated using several different methods. Usual internal treatment methods for white water at pulp and paper mills include filtration, flotation, and membrane techniques such as ultra-filtration. Also some evaporators can be found. Chemicals are used for purifying waters.

Prior to discharging waste-waters to recipients or even for re-use, biological purification methods are generally used. Chemical purification has been chosen in some cases as a secondary treatment. When striving to re-use biologically treated water, membrane filtration, usually ultra-filtration has been applied.

Most of the treatment methods cannot be applied without certain criteria for the water to be treated. As an example, there is a need to remove excessive solid matter from the waste-water before biological purification, and many other similar examples can be found. These needs are generally well known and thus regarded as self evident, but still sometimes forgotten.

A number of factors have emerged mainly on combining biological methods. One such issue has been the resulting impact of mixing different types of microbial masses. At an activated sludge plant, the sludge is separated by sedimentation and from the sludge which settles well, 98-99% is selected to recycle in the process. If, for example, the sludge coming from an aerated lagoon, is mixed with this sludge along with the incoming water, the sludge index in the activated sludge plant will rise, i.e. the sludge is bulking. Accordingly, the sludge starts to escape from clarification. There are results of this type of swelling in situations where there are equalizing basins or other “bioreactors” in front of the activated sludge plant.[15] In the design of equalizing basins, the production of bio-sludge has to be recognised, in order to keep it at a reasonable level. In practice, the level of produced bio-sludge without significant hazards should not rise above 200-300 mg/L. In the case of hazards emerging, the probable causes should be studied and, when required, the disturbing bio-sludge should be removed.

Also in some cases treatment of concentrates is a problem. Concentrated streams are now produced by membrane techniques such as ultra-filtration treating the white water from paper mills. Concentrations are quite high and lead to problems for other waste-water treatment processes. Problems most frequently arise from the fact that the topic has not been considered in the implementation planning.

I.3.8. Joint treatment with municipal waste-waters

Waste-waters from the pulp and paper industry have been treated with municipal waste-waters for a long time. Joint treatment pre-requisites will utilize the potential techno-economic benefits and will justify possible organizational obstacles. The benefits include cost factors and the opportunity use the plentiful phosphorus and nitrogen content of municipal waste-waters efficiently in the biological degradation of the organic matter in the pulp and paper mill waste-water. This opportunity provides technical and economic benefits especially for nitrogen removal which otherwise creates costs (Figure 3.7).

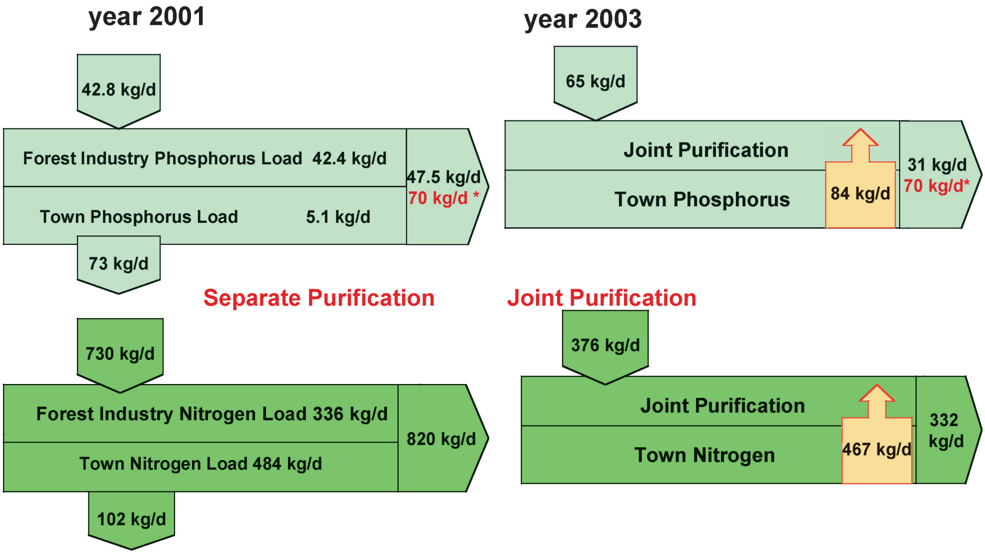


Figure 3.7. Changes in nutrient loadings when changing from separate treatment to joint treatment of a forest industry unit and the municipality[16]

The prerequisite of striving for efficient elimination of nutrients in the joint treatment of municipal and industrial waste-water is that the municipal waste-waters contain a little less nutrient than required to treat the industry's waste-waters. The study should be made using nutrient balance method and in successful joint treatments, significant reductions of nutrient emissions can even be achieved without considerable additional costs.[16]

The precondition of joint treatment is always the arrangement of economic matters in a manner satisfying both parties. The following obstacles have been observed to this activity or that require some contract provision:

- large fluctuations in the annual quantity of municipal waste-waters due to leakage from the sewer system,
- increasing area of the municipality and the resulting changes on the requirements for waste-water treatment,
- the industry's objective to increase production generally causing a rise in waste-water load,
- qualitative changes in the industrial production.

Joint treatment in several cases has provided very successful solutions but the technical and economic bases of the activity have to be clear and provisions made for change.

I.3.9. Comparative data of investment and operating costs

Investment and operating expenses of waste-water treatment have been gathered both by public authorities and by the industry. Handling of information for compilation of statistics has varied to some extent. OECD's calculation guidelines as well as different national calculation methods have been used for compiling statistics. In principle the calculation is simple, a summary of purification plant investments is made over a specified period of time and the resulting annual operating costs are determined. For the pulp and paper industry, however, environmental protection costs have often been the target. In this case the investment and operating costs of some process equipment and purification plant must be included. The most undisputed method would be a technical approach where the specification is made to define which equipment should be included in the calculations.

Companies have gathered information about the operating costs of treatment per cubic metre of treated waste-water or per waste units removed such as COD or BOD. The calculation must then include energy, chemicals, laboratory expenses, sludge treatment, and costs of work. The costs depend on the local price level. For example, data gathered in Finland have shown that the operating costs of mechanical-biological treatment are of the order of 8-12 cents/treated m^3. Deviations, even significant, exist from the figures above for various reasons.

When calculating investment costs, calculation methods must take into consideration working life-time and the interest charge used. Defining of, for example, exclusion of specific local features is important. In the instructions made, long inlet and discharge sewers have been ruled out of the cost calculation. Often this also applies to equipment belonging to the mill process such as heat exchangers.

In the calculation, 10-15 years is used as the working life-time for machines and equipment and 20-25 years for buildings and structures. The interest level to be calculated based on the local level. Due to the relatively complicated basis of the calculation it is understandable that companies can and have to make this type of calculation mainly for their own use. Comparison at a national level and adoption of approved calculation methods is more difficult. Comparison of different methods of treatment is demanding and requires adequate information about implemented solutions e.g. from the same geographical area and time.

According to the relatively little available information and by using slightly different calculation methods, investment costs of 9-15 cents/treated m^3 have been achieved for some cases of mechanical-biological purification in Finland in 2005.

References for Part I.3

1. U Hamm and S Schabel, *Effluent-free papermaking: Industrial experiences and latest developments in the German paper industry*, The 8th IWA Symposium on Forest Industry Wastewaters, Vitoria, Brazil, April 9-12, 2006 (on CD).
2. M Puukko, *Degree of closure of Nordic kraft pulp mills, 1990 and 2000-2005,* The 8th IWA Symposium on Forest Industry Wastewaters, Vitoria, Brazil, April 9-12, 2006 (on CD)..
3. G Tchobanoglous, F L Burton and H D Stensel, Wastewater Engineering. Treatment and Reuse, Metcalf & Eddy, Inc., revised by McGraw-Hill, 2003.
4. W W Eckenfelder Jr., Industrial Water Pollution Control, McGraw-Hill, 2001.
5. P Hynninen, P. Environmental Control, Papermaking Science and Technology, volume 19, Fapet Oy, Helsinki. 1998
6. M Teppler, P Nurminen, H Damen, J Kastensson and K Lundberg, *PM White Water Treatment at Metsä-Serla Kirkniemi Mill in Finland.* Paper presented at the Swedish Association of Pulp and Paper Engineers, Stockholm, Sweden, June 1-4, 1999.
7. G Pourcelly, *Presentation of the optimum and high efficiency wastewater treatment techniques in the different sectors of ILE. Membrane techniques.* ILE Guide Book. Section III, (2005).
8. J Chuboda, P Grau and V. Ottová, *Control of Activated Sludge Filamentous Bulking, II. Selection of Micro-organisms by Means of a Selector*. Water Res., 7, 1389, (1973).
9. N Stahl, A Tenenbaum and N I Galil, *Advanced treatment by anaerobic process followed by aerobic membrane bioreactor for effluent reuse in paper mill industry.* Wat.Sci.Tech. **50**(3), 245-252, (2004).
10. M Lerner, N Stahl and N I Galil, *Comparative study of MBR and activated sludge in the treatment of paper mill wastewater.* The 8th IWA Symposium on Forest Industry Wastewaters, Vitoria, Brazil, April 9-12, 2006 (on CD).
11. L Webb, *Effluent treatment heats up at mills*, Pulp & Paper International, **43**(4), (2001).
12. V Parravicini, K Svardal and H Kroiss, *Application of anaerobic biological treatment for sulfate removal in viscose industry wastewater.* The 8th IWA Symposium on Forest Industry Wastewaters, Vitoria, Brazil, April 9-12, 2006 (on CD).

References for Part I.3

13. L Habets, *Anaerobic treatment of pulp and paper mill effluents – Status quo and new developments.* The 8th IWA Symposium on Forest Industry Wastewaters, Vitoria, Brazil, April 9-12, 2006 (on CD).
14. L Webb, *Kidney technology brings success*, Pulp & Paper International 44 (4), (2002). Produced under an EU-funded program on “kidney technology”.
15. T Welander, T Alexandersson, T Ericsson and L Gunnarsson, *Reducing sludge production in biological effluent treatment by applying the LSP process,*. TAPPI International Environmental Conference & Exhibit, 757-763 (2000).
16. S Vatka, T Suomela and P Hynninen, Experience from the Joint Treatment of Forest Industry and Municipal Wastewaters with the Aim of High Nutrient Removal. Seventh International Water Association Symposium on Forest Industry Wastewaters, Seattle, USA, June 1-4, 2003, (on CD).

I.4. EMERGENT TECHNIQUES AND APPLICATIONS

New technologies used to treat effluents from paper mills are presented in this chapter**.**

I.4.1. Thermophilic biological treatment

Thermophilic methods are becoming interesting for the pulp and paper industry as a result of the continuously increasing white water temperature and energy prices. Aerobic plants have been studied for a long time (25-35 years) and a thermophilic anaerobic plant (an IC reactor from Paques) was installed a couple of years ago at a Dutch board mill, which already operated with a fully closed water system running at 50-60°C.

The objective of a European project (BRPR-98-8002) was to develop a suitable treatment technology (kidney technology) for closed cycle operation to realise effluent free paper production.
Two different approaches to the integrated treatment were investigated:

- pressurised thermophilic aerobic treatment with integrated biomass separation via membrane or flotation and,
- thermophilic anaerobic treatment combined with ultrafiltration.

The technology developed can be operated at increased temperatures enabling paper production at 55-60°C with significant positive effects on productivity (+5%) and energy consumption (> -5 %). Due to high biomass concentrations (20-25g/L), high temperatures and the use of membranes the treatment technology requires less space for installation. Waste production can be reduced sharply in relation to existing technologies (- 40 to-90%) and the specific COD loading rate of the biological stage is increased (> +50%) compared to conventional (mesophilic) treatment.

I.4.2. Electrochemical treatment

An electrochemical treatment process has been applied to the waste-water from the Charles Turner tissue mill near Bolton, U.K, which has installed a new tissue machine and associated de-inking plant. The mill previously had a conventional activated sludge plant following primary sedimentation, but this had to be dismantled to make way for the new paper machine. Instead of simply replacing the old plant with a new one, the mill decided to go for a relatively new and, at least on this scale, untested process using a very different technology.

After initial experimentation with electrochemical treatment of the raw waste-water, which worked but involved high chemical costs, the treatment sequence is now as shown in Figure 4.1. The first electrochemical cell uses iron electrodes and generates various free radicals that effect oxidation of the dissolved organics. Although this reaction is very fast (less than one second), a short retention time of 20 min. is provided after this stage and before the second electrochemical cell, which generates aluminium hydroxide from aluminium electrodes for coagulation of residual suspended solids. The final flotation stage is effected through the hydrogen gas generated in the second cell. Carry-over of plastics from the de-inking plant has caused some problems with cell operation, but these have been resolved through better upstream treatment and cell re-design. The incoming COD has been lowered from 250-350 mg/L down to as low as 40 mg/L with very effective removal of any colour from residual dyes.

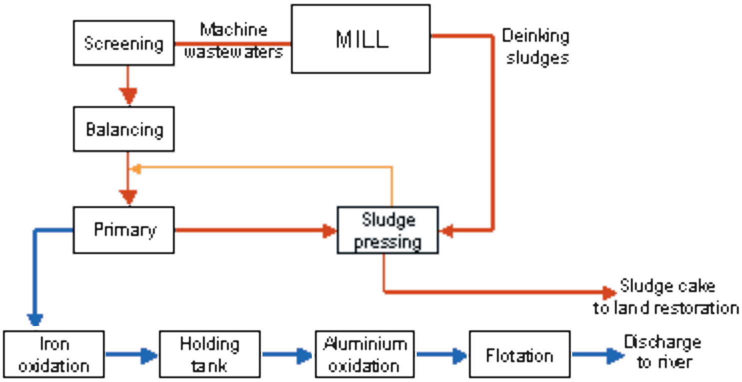


Figure 4.1. Electrochemical waste-water treatment process at a tissue mill

A key to the operation is the control of the power consumption in relation to waste-water COD and conductivity, but this is typically no more than 100 kWh/day. Both sets of electrodes do, of course, dissolve over time and have to be replaced about every three months. The operation of the plant is not yet fully optimized and some aspects of the operation cannot be divulged due to commercial confidentiality.

Another application of electrochemical treatment is at the Chartham mill of Arjo Wiggins Fine Papers, which has been evaluating a similar approach developed by Free Radical Technology (FRT). This process also generates free radicals in the water by means of one or more electrochemical cells and, as in any such technique, this may activate other ions in the system such as the oxidation of chloride to hypochlorite and oxygen to ozone. The process has so far been applied to deal with a problem that is not uncommon at many mills, namely odours from sludge handling.

The mill has a fairly conventional treatment process involving primary sedimentation followed by biological filtration with the surplus sludge being screw pressed. The press filtrate is returned to the primary treatment stage, but often in an anaerobic state which adversely affected process efficiency. Chemical treatment by chlorination was unable to rectify the problem. Electrochemical treatment was followed by retention for about 40 min. in a contact tank. Development of anaerobic conditions in the filtrate was prevented, odours eliminated and a substantial (over 1000 times) reduction in its microbial content achieved. Consistent efficiency has been obtained at an applied voltage of 5-6 volts with a current of 40 amps, i.e. power consumption of about 5 kWh/day.

I.4.3. Biological treatments

SCA Östrand pulp mill in Timrå (near Sundsvall), Sweden in April 2004, opened a state-of-the-art water purification plant that will radically improve the quality of water released into the environment. The new biological effluent treatment process at the plant involves treating waste-water from the pulp mill with microbiological organisms that break down organic matter in the waste-water. Compared with a typical effluent treatment works, the new Östrand "multi-bio" plant produces a lower total volume of effluent and processes the waste-water in about 12-14 hours, more quickly compared with the typical 24 hours. It also produces much less sludge.

MicroWeb MWR is a series of waste-water treatment equipment, designed to remove pollutants from waste-water rapidly and efficiently, combining with the proprietary MicroWeb technology of Tri-Y Technologies Inc. (Canada). This technology uses encapsulation/flocculation and a poly-complexed bridging mechanism to encapsulate, flocculate, adsorb, and stick the particles in the waste-water. Thus, the process is advanced, effective, and highly productive. After treatment, COD removal rate can be over 90%, and all of COD, BOD, SS, and pH can reach the discharge standards.

The M-real Lielahti CTMP mill in Tampere, Finland, expanded its biological waste-water treatment capacity in September 2002. The existing activated sludge system had insufficient capacity to serve the mill's needs. The mill bought a new treatment system using bio-film carriers a new technology that doubled its bioreactor capacity. Another activated sludge reactor with a similar capacity would have cost more than twice as much and would have needed more space. The water volume of the new bioreactor in Lielahti is 1,300 m^3, while a conventional system with the same capacity would have required a 7,000 m^3 operating tank. This was the first such bioreactor in Finland, although there are several installations worldwide. The chief engineer says that the system operates exactly as expected but has better operating stability than a "more technical" conventional system with rotating aerators. The system, which the supplier (MetsoPaperChem, a new unit of Metso Paper) calls FlooBed, has static aerators in the bottom of the tank. The new bioreactor contains an innovative system: microbes, which convert solid organic substance into sludge. The microbes are nurtured on plastic carriers, which float in the water in a mild nitrogen/phosphorus suspension. There are 6 million carriers in the 1,300 m^3 tank (4,600/m^3). The carriers have a large surface area to allow the microbes to settle, grow, and divide. With the carriers and aeration system, the efficiency of the new bioreactor is five times that of a conventional activated sludge system, considering the purification time or required tank volume.

Myllykoski, another Finnish company, recently opened Rhein Papier in Hürth, Germany (PPI, December 2002). The mill has a capacity of 280,000 tonnes/yr of newsprint made from 100% de-inked fibre and it has a special arrangement for its waste-water treatment. The mill has outsourced not only its maintenance, but several other activities as well, including part of its effluent treatment. The concept is that the waste-water is biologically pre-treated at the mill site and final treatment is done by a waste-water processing specialist in the (heavily industrialized) region. The waste-water treatment process includes a microflotation unit and two 750 m^3 FlooBed bioreactors from Metso. The waste-water passes through the system in four hours, during which time the COD is halved. Rhein Papier has no permanent employees in the waste-water plant, a laboratory technician takes water samples once per shift to track the BOD and COD content. The waste-water treatment is controlled from the paper machine control room. Rhein Papier uses 10 m^3 of water/tonne of newsprint and is satisfied with the operation. A long-term target is 7 m^3/tonne, but the first priority is a stable, high production level. The new bioreactor technology is considered mature and economic; the investment costs were lower than the traditional alternatives, and technologically the new system works very well as the carriers are good elements, and there is no wear at all, not even with the aerator system. All in all, the new system fits very well with the mill's overall business concept of minimizing labour.

I.5. PROMISING NEW TECHNIQUES OF TOMORROW

A number of emerging techniques have been shown to offer potential in the future.

I.5.1. Colour and chlorinated organics removal from pulp mills waste-water using activated petroleum coke[1]

The aim of this study was to investigate the production of activated carbon from petroleum coke. The activated carbon produced was applied for colour and AOX reduction from a bleached pulp mill waste-water.

The study describes all the steps of activated carbon production from petroleum coke and indicates that such carbon has adsorptive capacities 10 times higher than the raw coke. Several doses of activated coke were tested, with different activation times (ranging from 100-15000 mg/L). The results indicate that, in the dosage range of 100-2500 mg/L, the highest percentage removal of colour was about 33%, for an activation time of 4 h. Increasing the activated coke from 2500-15000 mg/L, colour removal increased up to 90%, for the same activation time. Similar trends were observed for COD, DOC, and AOX.

I.5.2. Sequential (anaerobic/aerobic) biological treatment of Dalaman Seka pulp and paper industry effluent[2]

In this study a pulp and paper industry effluent was examined for its toxic effects on anaerobic microorganisms. Additionally, the waste-water was treated in a sequential biological treatment process consisting in an anaerobic stage and an aerobic stage.

To investigate the toxicity for anaerobic microorganisms, bottles containing 10 cm^3 of inocula and different volumes of effluent (range 5-30 cm^3) were prepared. The gas production was monitored for a 14 days period. To assess the possibility of submitting the waste-water to an anaerobic biological treatment, a sample of the waste-water, (A), was fed to an UASB reactor with three hydraulic retention times: 34, 17 and 8.6 hours.

To consider the possibility of submitting the waste-water to a sequential biological treatment, a sample of the waste-water, (B), was fed to the UASB reactor plus a completely mixed stirred tank reactor. The UASB reactor was operated with hydraulic retention times of 8.6 and 5 hours, corresponding to 11 and 6.5 hours in the aerobic reactor.

The results indicate that the effluent had no inhibitory effect in the microorganisms under the studied conditions.

In the assay with the waste-water A, when the hydraulic retention times was 17 hours, the maximum COD removal (60%) and the maximum colour removal (46%) were achieved with 28% AOX removal.

In the assay with the waste-water B, the results indicate that the combined system improved the treatment 91% COD, 90% colour and 58% AOX were removed, at a hydraulic retention times of 5 and 6.5 for anaerobic and aerobic, respectively.

I.5.3. Batch and continuous studies on treatment of pulp mill waste-water by Aeromonas formicans[3]

The main aim of this study was to use a pure bacterial strain *Aeromonas formicans* for the degradation of black liquor in batch and continuous reactors in order to find out the efficiency of COD, colour, and lignin removal.

Batch experiments were carried out in 500 cm^3 Erlenmeyer flasks, containing 200 cm^3 of sterilized black liquor supplemented with nutrients, at an optimum concentration and pH value for *Aeromonas formicans*, to which was added 20 cm^3 of inocula to each flask. In addition continuous experiments were carried out in a completely mixed, continuous flow aerated reactors. These reactors had a 4 dm^3 capacity and were inoculated with 400 cm^3 of cell suspension of *Aeromonas formicans* and were operated with a hydraulic retention time of 8 days.

The results of the batch experiments indicate that, after 10 days, the removal of COD, colour and lignin remained almost constant. The reduction values achieved were: COD 71%, colour 86% and lignin 78%. The study also indicated that if cell concentration increased, the efficiency of treatment also increased. After 20 days of continuous flow reactor operation, the results showed that the removal efficiencies of COD, colour and lignin were 73, 87, and 76%. These values remained fairly constant on further addition of black liquor.

I.5.4. Remediation and toxicity removal from Kraft paper mill effluent by ozonization[4†3]

In this study, four different ozonization systems (O_3/pH3; O_3/pH11/H_2O_2; O_3/pH11; O_3/pH11/UV) were applied to a Kraft paper mill effluent. The purpose was to investigate the reduction of the following parameters: total organic carbon, total phenols, colour, and toxicity.

Four samples were prepared, one for each ozonization system. In each sample, the ozone concentration was 14 mg/L. In the O_3/pH11/H_2O_2 process the H_2O_2 concentration was 0.1 mol/L. In the O_3/pH11/UV process, ultraviolet radiation was provided by a high pressure mercury lamp (Philips HPL-N, 125 W, fluency rate 31.1 J.m^2/s^1 with the glass bulb removed).

The results showed for a 90 min reaction time that:

- the O_3/pH11/UV process was the most effective for decolouration (45%),
- the O_3/pH11 process achieved the highest phenol reduction (90%), but O_3/pH11/H_2O_2 and O_3/pH11/UV processes also performing well (70%),
- none of the processes showed significant TOC reduction (approximately 10% for O_3/pH11/UV and O_3/pH11 processes),
- the O_3/pH11 process was the most effective for the acute toxicity reduction (35%).

I.5.5. Purification of pulp and paper mill effluent using Eichornia crassipes[5†4]

With the aim of improving the treatment system of a pulp and paper industry, a new system using water hyacinth *Eichornia crassipes*, coagulation, and filtration has been developed.

The effluent was collected from the sedimentation tank of the existing treatment facility. The *Eichornia* reactor was tested at four flow rates (162, 216, 432, and 864 cm^3/min) and three plant densities (25, 30, and 35 g/L wet weight). Three parameters were considered: BOD, COD, and TDS. In the coagulation chamber two coagulants were used: lime (4 g/L) and alum (3 g/L). Three sand filters, with different bed depths (15, 30, and 35 cm) were tested in the filter unit. The results showed that the removal rate was inversely related to the flow rate and that a plant density higher than 30 g/L does not bring any benefits to the treatment. The removal rates, per hour, were 6.2% BOD, 5.2% COD, and 0.5% TDS. After filtration, the effluent turned almost colourless with 3.3 NTU of turbidity. After treatment, the metal content in the effluent was reduced to an undetectable level (<0.001 mg/L).

[†] See also Advanced Oxidation Processes – Section 3.

[†] See also Bioprocessing – Section 3.

I.5.6. Comparison of suspended growth system and hybrid systems for nitrogen removal in ammonium bisulfite pulp mill waste-water[6]

The aims of this study were to test the feasibility of total nitrogen removal from ammonium bisulphite pulping waste-water using bench-scale systems and to compare the stability of nitrogen removal between a suspended growth system and a hybrid system undergoing various operational conditions.

Two reactors with the same features and volume, 10 L, were constructed and operated for a 43 week period in a 4 compartment mode (1 anoxic zone and 3 aerobic zones) and for an additional 17 weeks using 6 compartment mode (2 anoxic zones and 4 aerobic zones). Both reactors were filled with activated sludge obtained from a pulping waste-water treatment plant. One of the reactors (reactor A) was operated only with suspended activated sludge during the experiment, while the other (reactor B) was charged with support media, in all zones, on day 75 of the assay.

At the beginning of the experiments, the two reactors were operated with a hydraulic retention time of 3 days and a solid retention time (SRT) of 50 days. The hydraulic retention time was later shortened stepwise to 0.5 day. The SRT was fixed at 10 days based for the remaining period. Results show that the organic removal efficiency is similar in both suspended and hybrid systems under the conditions tested. Stability under changing operational conditions, such as changes in the loading rate and recycle ratio, was an important factor in the overall nitrification process. In general, better stability was observed in the hybrid system. Higher total nitrogen removal efficiencies were achieved in the hybrid system than in the suspended growth system.

I.5.7. Mechanisms prevalent during bioremediation of waste-waters from pulp and paper industry[7]

The main goal of this paper is to review mechanisms prevalent during bioremediation of industrial waste-water, with special reference to the pulp and paper industry. Because the treatments of such effluents generated by this industrial sector, present particular problems that are often difficult to solve, bioremediation provides an important treatment methodology for this purpose. This paper investigates and focuses on techniques that are currently used to determine the efficiency of the bioremediation and mechanisms involved therein. For example the physiological significance of biosorption is examined and crucial questions surrounding the treatments of these effluents including efficiency of the technique used, its economic feasibility, legal requirements, etc. are also examined.

I.5.8. Conversion to fuel components

Levulinic acid can be produced economically from paper sludge and converted into an alternative fuel component, methyltetrahydrofuran, which can be used with ethanol and natural gas liquids to create a cleaner burning fuel.

I.5.9. Pyrolysis

Organic waste is heated in the absence of air to produce a mixture of gaseous and liquid fuels and a solid inert residue (mainly carbon).

A technology called SlurryCarb developed by the American company EnerTech has been funded by the US Department of Energy-Office of Industrial Technologies

I.5.10. Supercritical water oxidation

When heated beyond its critical temperature of 3740ºC and compressed beyond its critical pressure of 22 MPa (218 atmospheres), water acquires a new set of chemical characteristics. In this supercritical region of temperature and pressure, water can be used for supercritical water oxidation (SCWO). SCWO exploits the ability of supercritical water to dissolve both oxygen and non-polar organic compounds thereby allowing organic wastes to be oxidized into carbon dioxide and water. Compounds such as salts, usually soluble in ambient water, precipitate out of supercritical water and are available for recovery and reuse. Recent work carried out by Chematur Engineering suggests that SCWO has potential for recovery of fillers from de-inking sludge. This process can be used for highly toxic wastes.

I.5.11. Precipitated Calcium Carbonate

Specialty Minerals Inc. has developed a technology to produce a new "Recycled Mineral Filler Precipitated Calcium Carbonate" (RMF PCC), usable in the paper industry. When de-inking sludge is incinerated, typically at temperatures about 1,000°C, new mineral species are formed mainly composed of calcium aluminosilicate and calcium silicate minerals. All these minerals are suitable surfaces on which calcium carbonate will nucleate and grow during a precipitation process to produce precipitated calcium carbonate (PCC).

References for Part I.5

1. A R Shawwa, D W Smith and D C Sego, *Colour and chlorinated organics removal from pulp mills waste-water using activated petroleum coke* Water Res., **35**(3), 579-851, (2001)
2. U Tezel, E Guven, T H Erguder and G N Demirer, *Sequential (anaerobic/aerobic) biological treatment of Dalaman Seka pulp and paper industry effluent* Waste Management, **21**(8), 717-724, (2001)
3. Gupta, V.K., Minocha, A.K. and Jain, N, Batch and continuous studies on treatment of pulp mill waste-water by *Aeromonas formicans J. Chem. Tech. Biotechnol,* ***76**,(6), 547-552, (2001)*
4. R S Freire, L T Kubota and N Durán, *Remediation and toxicity removal from Kraft paper mill effluent by ozonization.* Env. Technol., **22**(8), 897-904, (2001)

References for Part I.5

5. S Yedla, A Mitra and M Bandyopadhyay, *Purification of pulp and paper mill effluent using Eichornia crassipes*. Env. Technol., **23**(4), 453-465, (2002)
6. J-H Seok and S J Komisar, *Comparison of suspended growth system and hybrid systems for nitrogen removal in ammonium bisulphite pulp mill wastewater***.** Env. Technol., **24**(1), 31-42, (2003)
7. B van Driessel and L Christopher, *Mechanisms prevalent during bioremediation of wastewaters from pulp and paper industry,* Crit. Rev. Biotech. **24**(2-3), 85-95, (2004)

I.6. HANDLING OPTIONS FOR PAPER SLUDGE

There are four main options for final disposal (in practice):

- burning,
- use for construction materials or making "constructions" for filling places etc.,
- agricultural use in some countries,
- land-filling.

The annual French production of paper sludges is 1.34 million tonnes: 0.72 Mt primary and biological sludges, and 0.62 Mt deinking sludge. The following handling options are used:

- spreading on land: 62%,
- incineration with energy recovery on-site: 22%,
- landfilling: 10%,
- cement industry: 4%,
- brick industry: 2%.

The performance of Finnish activated sludge plants (primary clarifier, equalization basin, buffer basin, aeration basin, secondary clarifier and sludge handling) was surveyed by the The Finnish Pulp and Paper Research Institute. Total sludge production at the paper mill plants averaged 40.9 t/d, 15% of which (5.9 t/d, 6.0 kg/t) was biosludge. At the pulp mills the figures were 27.2 t/d (11.5 t/d biosludge, 9.5 kg/tp). Belt filter presses are used for dewatering at most plants and dry solids contents are usually 25-35%. New-generation screw presses have been introduced, mainly at new pulp mill activated sludge plants, yielding dry solids content of 40%. Combined and dewatered sludge is normally burned in bark-fired boilers, although some mills still landfill their sludge.

In the U.K. around one million tonnes of paper sludge from recycling operations are generated annually, with these figures set to increase as paper recycling increases. Whilst a substantial fraction of the arisings are incinerated for energy recovery, a significant amount is also applied directly to land as a soil amendment, managed in accordance with an industry-wide code of practice.There are also some special and harmful wastes from pulp and paper mills: oils, recovery plant wastes, some chemical sludges etc.

Each year, the virgin and recycled pulp and paper industry worldwide produces approximately 20 million metric tonnes of residues from waste-water treatment and de-inking. De-inking residue consists basically of water (e.g. 50 %), organic matter (e.g. 25 %), and minerals (e.g. 25 %). Water is a resultant of the de-inking process. Organic matter consists of binders and fibres that are too small to be re-used in paper products. In the paper-making industry minerals, consisting in the majority of calcium carbonate and kaolin, with very well defined properties (e.g. purity and particle size) are used for various reasons of paper quality. Traditionally, paper mills deposit these residues in landfills or burn combustible residues and landfill the resulting ash.[1-3] Landfilling has several drawbacks: it consumes valuable space, may lead to long-term environmental problems, and wastes the potential value of the residues.

Sludge reduction and reuse within the papermaking process are key components required of paper mills as part of the European Commission Integrated Pollution and Prevention Control (IPPC) directive. The ultimate aim of a mill should be to minimize or eliminate discharges. Paper mills are faced with the task of using increased levels of secondary fibre, recovering and recycling the fibre and reducing paper sludge generation.[4]

With waste reduction and reuse strategies in place, waste hierarchy principles advocate a number of options described as ‘recovery’:

- sludge stabilization techniques such as composting,
- recycling as construction materials,
- energy recovery with sludge destruction.

I.6.1. Sludge stabilization

I.6.1.1. Composting

There is no evidence that paper sludge alone can be successfully composted, due to the high carbon to nitrogen ratio in primary sludge. However, mixtures with absorbent materials/bulking agents such as straw and bark combined with nitrogen containing animal manure have been shown to compost readily.[5] Composting is acquiring greater significance as a waste management option.

The chemical characterization of paper sludges and their young (immature) compost was investigated at the Laval University in Quebec, Canada. Over 150 inorganic and organic chemicals were analyzed in de-inking paper sludge (DPS). In general, nitrogen, phosphorus and potassium contents were low but variable in raw DPS and its young compost. The contents of arsenic, boron, cadmium, cobalt, chromium, manganese, mercury, molybdenum, nickel, lead, selenium, and zinc were also low and showed low variability. However, the copper contents were above the Canadian compost regulation for unrestricted use and required a follow-up. The organic chemicals measured at the highest concentrations were fatty- and resin acids and polycyclic aromatic hydrocarbons. In the case of resinic acids, care should be taken to avoid leachates reaching aquatic life, and for polycyclic aromatic hydrocarbons, naphthalene should be monitored until soil content reaches 0.1 μg/g, the maximum allowed for soil use for agricultural purposes according to Canadian Environmental Quality Guidelines. In young compost, the concentration of these chemical families decreased over time and most compounds were below the detection limits after 24 weeks of composting. In raw DPS, among the phenol, halogenated and mono-aromatic hydrocarbons, dioxin and furan, and polychlorinated biphenyl families, most compounds were below the detection limits. Thus raw DPS and its young compost do not represent a major threat for the environment but can require an environmental follow-up.

Co-composting dewatered paper mill sludge (PMS) and hardwood sawdust, two readily available materials in Canada, was investigated using uncontrolled and controlled in-vessel processes. The co-composting of the PMS and hardwood sawdust can be successfully achieved if aeration, moisture, and bioavailable C/N ratios are optimized to reduce losses of N.

The feasibility of aerobic vessel composting and anaerobic digestion for the treatment of pulp and paper mill sludges was studied. The composting studies made use of primary and secondary sludge from a de-inking and paper mill in Finland. The study showed that pulp and paper mill sludges are amenable to both aerobic composting and anaerobic digestion.

Paper mill sludge is usually composted in the U.S. and Canada by blending with organic wastes such as sawdust and animal manures, placed in windrows, and allowed to compost for three to five weeks with frequent turning of the windrows. Completely cured compost that is acceptable for containerized plant production can be achieved by maintaining the compost in a static phase for an additional four to six weeks with occasional turning.

I.6.1.2. Anaerobic digestion

Historically this practice has been associated with the treatment of animal manure and sewage sludge from aerobic waste-water treatment plants. By definition, anaerobic digestion requires that the given waste/waste-water contains a substantial amount of organic matter so that it can be converted (in the absence of oxygen) to methane, CO_2, and biomass. However, recent, high-rate reactor configurations and sophisticated process control have allowed anaerobic digestion to enter areas that were dominated by aerobic systems such as the treatment of industrial effluents with low COD levels.[6] But this process is not widely used in the paper industry.

I.6.2. Construction materials and cement

It is technically feasible to use paper mill sludge in a range of different applications in the construction industry. However, barriers exist to prevent the immediate adoption of this possibility including:

- the costs of virgin materials are as low as industrial alternatives,
- lack of standards, specifications and regulations,
- concerns over future liabilities,
- costs involved in testing,
- the unlikelihood that all sludge produced can be reused,
- lack of demand for more industrial wastes to be used as raw material for construction products or as a source of fuel.

There have been many attempts to use incinerator ash in the cement industry. Since the early 1990s the Wopfing Cement Works in Austria have practised a new technology for a 50,000 tonnes/year fibre residue that has proved to be reliable. It utilizes the calorific value of the dried fibres, and the high ash content of the fibre residues provides an excellent raw material for the production of cement clinker.

Dutch paper mills annually produce about 300,000 tonnes of de-inking residue. Four Dutch papermills: **C**eltona, **D**oetinchem, **E**det, and **M**ayr Melnhof joined together to form CDEM Holland BV in the early 1990s with the sole goal of replacing the landfilling of de-inking sludge by an environmentally more sound solution. CDEM developed a proprietary (patented) process that allows the production of a new type of admixture for use in building materials. The process consists of controlled thermal conversion of de-inking paper residue in a fluidized-bed combustor. The resulting mineral product (TopCrete) presents both hydraulic and pozzolanic properties. The plant opened at AVR-AVIRA in Duiven (The Netherlands) and is able to treat 200,000 tonnes of paper pulp residue per year.

Research is continuing in the UK and Germany for the recycling of mill waste (sludge or filter cake) into high temperature insulation bricks. One project funded by the US Environmental Protection Agency (EPA) studied the conversion of mill waste into a composite activated sorbent which can then be used to purify industrial waste-water. Another EPA project involved incorporating fibrous residuals from mills into ready-mixed concrete to improve the strength, durability, and life span of concrete structures.

I.6.3. Incineration with energy recovery

Incineration is becoming a more widely used waste management option: burning waste to generate electricity for use at the plant and to sell to the national grid. Paper sludge has already been used as a fuel source in many plants and is generally mixed with barks of trees. The volume of ash from incineration processes is significant: typically around 25 % of the total amount. Disposal of incinerator ash is a problem that is becoming increasingly important.

References for Part I.6

1. J Pickell and R Wunderlich, *Sludge Disposal: Current Practices and Future Options,* Pulp & Paper Canada, **96**, 9, (1995).
2. I D Reid, *Solid Residues Generation and Management by Canadian Pulp and Paper Mills in 1995*, Paprican Miscellaneous report 352, (1997).
3. L Webb, *A Host of Options Available for Sludge*, Pulp and Paper International, **38**, 11, (1996).
4. M Kay, *What to do with sludge?* Pulp and Paper International, **45**, 8, (2003).
5. T Arrouge, C Moresoli and G Soucy, *Primary and Secondary Sludge Composting: A Technico-Economical Study,* 84th Annual Meeting, Technical Section CPPA, Montreal, Canada, (1998).
6. R Steffen, O Szolar and R Braun, *Feedstocks for Anaerobic Digestion,* Institute for Agrobiotechnology, Tulln University of Agricultural Sciences Vienna. (1998)

I.7. CONCLUSION

This guide-book gives a general overview of the pulp and paper (P&P) industry and its typical effluents, especially water. High organic matter content is the major characteristic of P&P mill effluents. As the P&P sector uses 11% of the total volume of water used in industrial activities in OECD countries, it requires particular attention. Water is required in large amounts and must meet certain minimum purity criteria and as the amount of fresh and waste-water is approximately the same, recycling steps are necessary. After pre-treatment, the efficient external waste-water treatment techniques available for use include both primary and secondary treatments, the latter usually biological. Pre-treatment is necessary for physico-chemical standardization (screening, pH, and temperature adjustments). Primary treatment is generally used to reduce heavy sediments (through for example sedimentation or flotation of the solids) with addition of coagulation and flocculation reagents. Secondary treatment is used to remove colloidal or dissolved organic matter together with some inorganic compounds (aerobic or anaerobic processes, chemical precipitation). In some cases, a polishing step (tertiary treatment) is needed, such as subsequent filtration, clarification, flotation, biological treatment.

Some P&P mills have adopted the concept of closed water loops and do not have any biological treatment. However, closed water circuits do not necessarily mean optimum environmental performance. The accumulation of contaminants needs specific treatment processes with sometimes high energy consumption. Pressure-driven membrane processes (micro- ultra- and nano-filtration), vacuum evaporation, ozone treatment, direct biological treatment requiring cooling systems can be involved in such a concept.

Currently, the necessity of reducing fresh water consumption is promoting new technologies such as thermophilic aerobic treatment involving a membrane bioreactor, electrochemical process where electrode reactions generate free radicals to oxidise dissolved organics, new biological treatment with bio-film carriers, or wet air oxidation process.

In the future, some of the promising techniques which are presently at the lab-scale will be involved in the treatment of P&P waste-waters. Most of them concerns biotechnologies, natural materials such as petroleum coke, ozonization, partial spray freezing or membrane bioreactors.

The absolute necessity to reduce water consumption in the P&P industry, the increasing pressure of environmental constraints, the goal of a zero-reject industry are many reasons to develop new concepts which could then be included in other high consuming water industries. This is the vision for tomorrow.

Acknowledgement: Professor Pertti Hynninen, Enviro Data, Finland, is thanked for his critical review of this report from the Pulp and Paper Industry Cluster.

II.

INDUSTRIAL LIQUID EFFLUENTS IN MINING AND METALLURGICAL INDUSTRIES

Cluster Leader

University of L'Aquila, Dept. of Chemical Engineering and Materials, Italy - M. Pelino.

Members

National Technical University, School of Mining and Metallurgical Engineering, Athens, Greece - M. Tsezos.

University of Hertfordshire, School of Life Science, U.K. - M. Cox.

RWTH Aachen University, Dept. of Ferrous Metallurgy - K. Mavrommatis.

La Sapienza University, Dept. of Chemical Engineering, M.M.P.M., Rome, Italy - C. Lupi.

INDEX

INTRODUCTION*

Mining and metallurgical processes, during operation and after site decommissioning, generate solid wastes and liquid effluents that need to be treated before discharge to the environment.

The mining processes involve the disruption of the immediate environment of the mine since the extraction process entails the removal of large amounts of material. The environmental impact on mine sites is generally large, with total destruction of the vegetation of mined areas, and considerable reshaping of the natural topography. The removed materials together with the mining tailings become waste streams.

Under old mining methods, once a mine became uneconomic, it was abandoned with little or no attempt to rehabilitate the land. The mining industry still suffers from the negative public image resulting from centuries of neglectful practice. Today, developed nations generally have stringent guidelines to ensure the rehabilitation of mined areas in order to restore the site to as close as possible to the natural conditions. Moreover, most of the European and North American mining companies are committed to employ the same environmental protection practices in overseas operations, even though the regulations in other countries are not as strict.

One of the major impacts of mining is to bring to the surface large quantities of minerals that are unstable in the weathering conditions. In particular, sulfide minerals in waste rocks and tailings react to form sulfuric acid (H_2SO_4). Run-off from mines may also have enhanced levels of metals such as arsenic, copper, lead, iron, cadmium, and nickel. When the mine is decommissioned, the combined action of the mine waters pumped out during operations, oxygen and bacteria generates acid mine drainage (AMD) with resulting high acidity (pH 2) and metal concentration (3-5 g/L of Fe, Cu, and sulfate) that can be devastating for the ecosystem, far away from the mine site.

Ore treatment processes also produces liquid effluents polluted by cyanide, kerosene, organic flotation agents, activated carbon, and sulfuric acid. Smelting and refining generates air pollution with nitrogen and sulfur oxides and particulates (dusts) rich in vaporised metals. When the recovery of metals (Zn, Pb, Ni, Cr) from electric arc furnace dusts (EAFD) is carried out by one of the several hydrometallurgical processes, large amounts of polluted water are generated and must be treated before recycling in the plant or re-emission into the environment.

During the last 20 years, regulation of water disposal from metal-working operations has become more and more rigorous. Previously water treatment mostly involved end-of-pipe treatment, where the total discharges from a facility were treated without regard to the source of the water within the facility. Conventional treatment involved chemical/physical processes where soluble components were first chemically precipitated, and the resulting colloidal components, together

---

[*] Report prepared in association with Paola Pisciella, University of L'Aquila.

with any other suspended contaminants, were flocculated. The water would then be passed into a clarifier, where the sludge was removed and pumped through a filter press for dewatering and the clarified water discharged. The system was expensive to operate, since labour requirements and chemical and disposal costs were high. First, and most importantly, "end-of-pipe" treatment has largely been replaced by point-source treatment allowing removal of contamination from heavily loaded effluents with several small treatment systems carrying out the operation required by the whole facility, resulting in more cost-effective procedures.

It is worth highlighting that, due to the large volume of polluted water generated by decommissioned mining sites or arising from metallurgical operations, the applied water treatment technologies are mature, economically convenient, and exchangeable with other industrial sectors.

The Mining and Metallurgy section of the Industrial Liquid Effluents Guide Book begins with an inventory of the European mining sites: the main source of information is the report *BRGM (2001): Management of mining, quarrying, and ore-processing waste in the European Union.* The production of mining wastes and liquid effluents is related to an overview of the principal mining and mineral processing operations; a description of the characteristics of liquid effluents generated by each activity is presented. Due to the absence of a systematic monitoring of water characteristics in the active and abandoned mining sites in Europe it is not possible to present a detailed and global characterisation of the waste-waters generated by mining.

The principal metallurgical operations are described and the characteristics of the waste-waters presented. The water treatment techniques are classified as: applied waste-water treatment techniques, conventional treatments, and emerging techniques and applications.

II.

CHAPTER II.I: MINING

II.I.1. INTRODUCTION: ENVIRONMENTAL PROBLEMS ASSOCIATED WITH MINING ACTIVITIES

II.I.1.1. Inventory of European mining sites

Metallic ores mined in the European Union are concentrated in the following regions:

- the Mediterranean (Portugal, Spain, Greece),
- Ireland, the leading European country in the production of zinc and lead,
- Sweden and Finland, particularly in Scandinavia with the Baltic shield.

In France, Germany, Italy, U.K., and the Benelux countries, nearly all the metallic mines have been shut down or anticipate closure.

Europe currently retains a modest position in world mining activity in terms of scale of production and mineral reserves, (Table I.1) but maintains a significant role in the world mineral industry due to the fact that many companies are domiciled in Europe, often in London. Thus although within its frontiers production in the mineral industry is modest, Europe preserves a major role in the management of world resources on the international market. In addition, many engineering organisations and equipment manufacturers are located in Europe[1].

Substance	Units	Quantity	% world reserves
Antimony	Kt (Sb)	440	10.5
Arsenic[1]	Kt (As)	180	18
Asbestos	Mt	51	30
Barite	Mt	36	20.5
Bauxite	Mt	1642	7.1
Beryllium	Kt (Be)	61	16.3
Bismuth	Kt (Bi)	0	0
Chromium	Mt (Cr_2O_3)	47	2.9
Cobalt	Kt (Co)	140	3
Copper	Mt (Cu)	53	17.1
Diamonds	Mct	200	19.2
Fluorine	Mt	90	42.9

Substance	Units	Quantity	% world reserves
Gold	Kt (Au)	3	7
Iron	Mt (Fe)	26650	38.1
Kaolin	Mt	2865	14.6
Lead	Mt (Pb)	20	31.7
Lithium	Kt (Li)	0	0
Manganese	Mt (Mn)	142	21.8
Mercury	Kt (Hg)	96	73.5
Molybdenum	Kt (Mo)	241	4.4
Nickel	Kt (Ni)	7050	15.7
Niobium	Kt (Nb)	680	16.1
Phosphates	Mt	670	5.6
Platinum	t (Pt,Pd)	14010	21.2
Potash	Mt (K_2O)	4455	47.3
Rare Earth[2]	Kt (REOxide)	19050	19.1
Silver	Kt (Ag)	73	26.1
Sulfur	Mt (S)	500	35.7
Talc	Mt	90	20.5
Tantalum	Kt (Ta)	2	7.3
Tin	Kt (Sn)	325	4.5
Titanium	Mt (Ti)	50	16.2
Tungsten	Kt (W)	355	16.1
Uranium[2]	Kt (U)	60	2.8
Vanadium	Kt (V)	5005	49.6
Zinc	Mt (Zn)	19	10
Zirconium	Mt (ZrO_2)	4	12.5

(1) arsenic present in lead and copper ores; (2) in oxide equivalent, including yttrium.

Table I.1. European mining reserves (including Russia and Ukraine) of different substances (Source: BRGM (2001): *Management of mining, quarrying, and ore-processing waste in the European Union)*

Table I.2 indicates the number of mining sites, including those known abandoned or closed, included in BRGM (2001): Management of mining, quarrying and ore-processing waste in the European Union.

Four main categories of ore were considered into which all extracted substances, within the scope of the study, can be placed: ferrous metals; non-ferrous metals; industrial minerals; coal.

Country	Ferrous metals		Non-ferrous metals		Industrial minerals		Coal	
	total sites	closed sites	total sites	closed sites	total sites	closed sites	total sites	closed sites
Austria	2		1		>500*		2	
Belgium	>500	all	>300	all	>4700	>4500	>4000	all
Denmark	local	closed	a few		opencast		lignite	closed
Finland	5	5	38	26	12	7		
France	17	17	160	158	119	77	81	77
Germany	3	1	3	3	105	1	44	2
Greece	3		6	1	15	1		
Ireland			21	`7	6	4	4	4
Portugal	8	7	9	9			1	1
Spain	20	18	58	45	47	20	73	25
Sweden	3		20	14				
U.K.	36	36	31	29	22	?	23	?

* most sites related to aggregate production

Table I.2. Number of mining sites within European Union countries (Source: BRGM (2001): *Management of mining, quarrying and ore-processing waste in the European Union)*

This table should not be interpreted as representing all sites in the European Union but it is the result of the above study and it has to be considered a first attempt to carry out an inventory at the European level.

The final stages of mining exploitation typically involve the closure of the mine, implementation of reclamation and environmental requirements associated with the cessation of mining operations, and the liability associated with mine wastes that extend beyond the life of a given project. Within this context, the potential impact of mining operations and their cessation on the quality of water resources is a primary concern in local communities. In many mining regions, even in some arid environments, pits may intercept ground-water, and require pumping during exploitation. When mining has ceased, these pits will refill nearly to the historical ground-water level, but the water quality will deteriorate. The chemistry of mine waters has been studied by several authors[2,3] with most of the attention being devoted to acid mine waters, since these usually carry huge amounts of metals, and cause impressive visual impacts. However, methods for assessing the quality of pit water, how it affects the surrounding ground-water, and how long adverse affects will persist are currently inadequate.[4]

In Europe, most mines have been closed for economic reasons over the past decades with now more than half the mining sites within the E.U. closed. In most regions mine closure implies the cessation of expensive pumping systems. The rise of deep saline waters, as a consequence of planned mine flooding, prompted the assessment of the contamination risk for shallow ground-water. Water demands in the southern areas of Europe exceed water reserves, and restrictions on the water supply are frequent, especially during the summer. Therefore waters are regarded as an important potential resource. In fact recently, shallow ground-water from mines has been often used, after mixing with better quality water, to supply towns in the southern areas of Italy and Spain. Companies managing the mines, in some cases carry out projects for monitoring water level and some chemical parameters. Several studies have been carried out with the objectives of investigating the geochemical properties of the mine waters and related ground-waters to monitor water quality prior to and during mine flooding, and to assess the contamination risk for shallow ground-water.[5]

It is obvious that the concept of sustainable development related to environmental protection has not always been sufficiently considered, particularly in the past. As a consequence, a distinction should be made between the following types of mines:

- abandoned/old mines,
- operating mines substantially based on old designed operations,
- operating mines based on new design and technology.

Serious problems are arising from abandoned mines and mines in which the activity was based on old operations which have been conceived without appropriate environment management. There is a need of basic criteria for mine closure plans, based on approaches such as defined by European working groups like CARACAS (Concerted Action on Risks Assessment for Contaminated Sites) or CLARINET (Contaminated Lands and Risks Network for European Technologies).[1]

II.I.2. OVERVIEW OF MINING AND MINERAL PROCESSING OPERATIONS

The production of minerals for economic use involves a series of physical and chemical processes. These may occur at any time from the excavation of the ore containing the metal in mineral form through to production of the metal in a marketable form.

Several factors including location, geometry, morphology, depth, economics, environment, and even mining tradition underlie the choice of method(s) for mining a specific ore deposit. Depending on the chosen method, and on the size of the mine site, projects will display different ore-extraction capacities, and consequently larger or smaller quantities and different types of waste and consequently waste-management methods.

Open pits and quarries[1]

There are many alternatives within open pits and quarries but the general principles are identical. Most industrial materials and shallow metallic deposits (< 300 m) are mined by this method, which is the cheapest in practice. The scale of the projects, and particularly their depth, is conditioned by an economic threshold above which it is better to continue mining through underground workings.

As a rule, after the stripping operations to remove the soil and superficial horizons, actual mining is carried out in successive steps, imparting a roughly conical shape to the mine. The mining of each step or bench produces a tonnage of extracted material corresponding to the overburden surrounding the deposit, which is sent directly to the waste dump, and a tonnage corresponding to the ore that is selectively routed either for storage or directly to the processing plant. The variation in the ratio between the tonnage of waste to be extracted and the quantity of ore recoverable, also called the stripping ratio, strongly conditions the economic viability of the mine. If this ratio becomes too high, especially when the quarry is deepened, it is no longer economically profitable to continue strip mining.

Underground quarries and mines[1]

When deposits are difficult to reach from the surface due to for example depth or cliffs inhibiting side access, the only alternative is underground working. A broad range of methods are available all of which are roughly adapted to the characteristics of the ore or the geometry of the deposit. This method of mining when compared to surface quarries has the following characteristics:

- ore extraction capacities are generally much lower,
- quantity of waste produced per unit of ore mined is much lower,
- ground area is considerably smaller than for surface quarrying, except for sub-horizontal layers.

II.I.2.1. Mining phases and operations[6]

The operations carried out on a mine site to exploit and upgrade a deposit can be divided into three main steps:

- mining (or “extraction”),
- beneficiation (e.g. milling and leaching),
- mineral processing (e.g. smelting and refining).

Each of these ore-mining and processing steps can generate waste that generally has different physical and chemical properties, resulting in different potential environmental impact. The respective volumes of waste produced depend essentially on the type of deposit and the technological alternatives used for mining and for ore processing; thus in strip-mining removal of the deposits often produces the most waste during ore extraction. The chemical composition of the waste varies considerably according to the substance mined and the nature of the geological formation containing the deposit.

Each subject in this chapter begins with a discussion of the process followed by a discussion of wastes generated. It is worthwhile noting that the three types of operations may or may not be located on the same site.

II.I.2.1.1. Mining

The initial step of the mining and mineral processing operations is the removal of the mineral value in ore from the host rock or matrix. Minerals may be extracted from the ground using a variety of techniques. Most extraction processes remove the ore and associated rock or matrix in a bulk form from the deposit, using blasting followed by various mechanical means to break the ore into pieces of manageable size, or to separate the ore minerals from unwanted material. The largest quantity of waste generated by extraction operations are mine water and waste rock. A third waste material, overburden, is generated at surface mines.

Mine water is defined as water entering a surface or underground mine from sources such as ground-water seepage, surface water inflow, or direct precipitation. In the absence of natural or man-made drainage, active mine operations below the water table must pump out this mine water to access the ore body. At some mines enormous quantities may have to be pumped continuously from the mine during operations. Active mines may use the mine water for dust control and as process water in the mill circuit; otherwise it is typically discharged to surface water under appropriate permits and licences. Mine water discharge from operating mines is typically regulated and often does not have sufficient residence time within the ore or mine to create highly acidic waters or waters highly loaded with dissolved metals. However, the need to treat mine water prior to discharge is highly site specific.

When a mine closes, dewatering the mine generally ceases. Thus underground mines often refill with water and mine water may be released through openings or fractures and fissures that reach the surface. If present, man-made gravity drains will continue to flow. Surface mines that extend below the water table will return to that level when pumping ceases, either forming a lake in the pit or inundating and saturating fill material.

Water from abandoned mines may contain significant concentrations of heavy metals and total dissolved solids and may have elevated temperatures and altered pH values, depending on the nature of the ore body and local geochemical conditions. These waters may become acidic over time when exposed to oxygen and, if present, pyrites or other sulfide minerals. Such acidic water may also solubilize metals contained in the mine and mined materials, creating high concentrations of metals in solution. These acidic metal-laden waters may then contaminate ground-water and surface water resources. Neutral and alkaline mine waters may also contain metals in excess of water quality standards and be of significant concern to human health and the environment.

II.I.2.1.2. Beneficiation: Milling

Following the initial mining step, ore is reduced in size by the crushing and/or grinding circuit, and then the target mineral is concentrated by various methods. These widely varying concentration processes are collectively referred to as beneficiation. Beneficiation activities generally do not change the mineral values themselves other than by reducing, e.g. crushing or grinding, or enlarging, e.g. pelletizing or briquetting, particle size to facilitate processing. Generally, no chemical changes occur in the mineral values during beneficiation. The purpose of ore beneficiation is the separation of valuable minerals from the gangue to yield a product that has a much higher content of the valued material. The wastes generated by beneficiation milling operations are collectively known as tailings.

Unused or discarded chemicals associated with these beneficiation operations at historic mining sites may also remain on-site and need to be managed during remediation. These could include: mercury at sites that have used amalgamation, and chemicals used in flotation such as copper sulfate, various amines, and sodium cyanide. Tailings disposal is a significant portion of the overall waste management practice at mining and milling operations. The method of disposal of tailings is largely controlled by their water content. Generally, three types of tailings based on their water content may be identified: wet, thickened, and dry. Although the tailings have much lower concentrations of the target mineral(s) than the mined ore, they may be a source of contamination at the site due to the presence of sulfides such as pyrite (acid generation), metals (available for mobilization in ground or surface waters), and reagents added during beneficiation. Tailings that are fine grained and managed under drier conditions are especially prone to producing dust. Sulfide tailings oxidized by weathering are potential generators of acidic run-off.

In the past, and currently in some other countries, tailings often were disposed wherever convenient, for example, into rivers if flow was sufficient, held behind dams if necessary, or placed on land. Tailings now are managed, in a wet or thickened state in tailings impoundments, or dry in disposal piles. In addition to placement in managed units, certain tailings may be slurried as backfill into underground mines. In some cases efforts to backfill or seal the mine could increase the risk of generating acid mine drainage (AMD).

An alternative method of tailings disposal is underwater in a permanent body of water, such as a lake, ocean, or an engineered structure e.g. a pit or impoundment. This has been an historical management practice and is still practiced in some countries e.g. Canada. The potential advantage of underwater disposal of tailings is the inhibition of sulfide minerals oxidation, thus preventing or slowing acid generation. Substantial uncertainty exists regarding other short- and long-term effects on the water body into which the tailings may be deposited.

II.I.2.1.3. Beneficiation: Leaching

Leaching is the process of extracting a soluble metallic compound from an ore by selectively dissolving it in a suitable solvent, such as water, sulfuric acid, or sodium cyanide solution. The target metal is then removed from the ”pregnant” leach solution by one of several electrochemical or chemical means.

Ore may be crushed or finely ground to expose the desired mineral prior to leaching. The tailings from other beneficiation processes, such as flotation, may also be leached to remove additional metal(s).

Dump and heap leach waste.

Following leaching, the large amounts of spent ore that remain are usually left in place. These piles of leached ore vary widely in size; the largest covering hundreds of acres, rising to several hundred feet, and may contain tens of millions of tons of leached ore. Alternatively, the leached ore from smaller leach pads may be moved to a dedicated dump for additional and long term dump leaching. Uncollected leachate from these piles is a potential source of contamination of ground water, surface water, and soil. In addition, other contaminants notably, arsenic, mercury, and selenium, but also including many other heavy metals present in the spent ore may appear in the leachate over time. Acid drainage may be generated from the oxidation of sulfide ores and requires control.

II.I.2.1.4. Mineral Processing

Following the above beneficiation processes to concentrate the mineral value, the concentrate typically is processed to further extract and/or refine the metal, thus preparing it for its final use or for incorporation into physical or chemical products. There are a variety of mineral processing operations, including the following major categories: pyrometallurgical operations e.g. smelting, refining, roasting; hydrometallurgical operations e.g. leaching, solution purification and electrometallurgical operations e.g. electrolytic refining. Each of these mineral processing operations generates its own specific waste streams.

Various process waste-waters are and have been generated during various pyrometallurgical operations. Historically, these have been co-managed with tailings if the smelter or refinery was conveniently located. In other cases, discharge to surface waters or surface impoundments was the preferred approach.

II.I.3. CHARACTERISTICS OF LIQUID EFFLUENTS GENERATED BY MINING

Mining and metallurgical processes, during operation and after site decommissioning, generate several types of acidic and toxic effluents that are treated before their discharge to the environment. These effluents include:

- mill tailing excess decant (or reclaim tailings water),
- process acid streams,
- acid mine drainage and seepage, (AMD).

Reclaim tailings waters have either neutral or high pH, contain <20 mg/L total dissolved metals, and so polishing with lime is usually sufficient to comply with regulatory limits.

Process acid streams originate from the use or generation of acids during metallurgical processes, such as barren solutions, spent electrolytes and weak acids, and recycled process waters.

Natural oxidation of sulfide minerals present in mine wastes, tailings and waste rocks results in the occurrence of AMD that is characterised by low pH, highly acidic effluents containing heavy metals and sulfate[7]. As control of AMD generation from mining activities is not yet a common practice, treatment of AMD is necessary to meet regulated water quality standards. AMD control technologies are measures that can be undertaken where formation of AMD has either already taken place or is anticipated to be a problem in the future. At-source control methods treat the acid-producing rock directly and stop or retard the production of acidity, whereas treatment methods add chemicals directly to acidified water exiting the rock mass. It is obvious that cost effective methods that prevent the formation of AMD at its source would be preferable.[8] Among the investigated control methods alkaline additions and the Bauxsol technology have to be highlighted.

Water pollution may appear at different stages in the management of tailings. For example, failure of the discharge may cause spills and damage the surrounding environment. Alternatively, rain and process water may create leachates when passing or seeping through tailings, particularly in respect of tailings from ferrous and non-ferrous ores, giving rise to:

- sulfide oxidation and potential acid generation,
- sulfide oxidation and production of soluble salts,
- metal leaching and migration into the surrounding environment,
- leaching of residual process chemicals in the tailings, e.g. cyanide, acids, alkalis,
- geochemistry and toxicity of the waste materials impacting on humans, vegetation and fauna.

These can also result from:

- seepage through and below impoundment walls,
- percolation to the subsoil and ground-water,
- overflow of the dam walls or spillways.

Moreover it should not be forgotten that, as mentioned above, one of the methods of the disposal of tailing is into deep water, although it is rapidly becoming non-authorised as a standard practice.[1]

II.I.3.1. Quantities of waste-water generated by mining operations

The absence of a systematic monitoring of water chemical analysis and loading in the principal mines in Europe renders it impossible to characterise the waste-water generated.

Estimation of the amount of the polluted waters generated after mining closure needs the knowledge of the post-mining hydrology; the hydrology of a backfill and its effect on AMD are very complex, but research on the movement of water into and through a mine backfill provides information on preventing and controlling AMD.

In a recent study, carried out on the AMD formation in a closed pyrite mine in Italy, Tuscany, it has been evaluated that iron and sulfate release into surface water amounts to 0.7t/d and 1.2t/d respectively.[9]

It is clear from this background, that to estimate the total quantities of waste-water generated by mining operations is difficult. However the liquid effluents coming from tailings, drainage, and seepage are directly related to the solid wastes. In the European Union study BRGM (2001): *Management of mining, quarrying, and ore-processing waste in the European Union*, an estimation of the amount of solid waste generated has been made based on production. This estimation was established starting from known data concerning the production of metal ores and industrial minerals within the European Union between 1986 and 1995.

The following table I.3 present the results of the estimation for ferrous and non-ferrous ores over a 10 year period. This table should be read carefully because the ratios are presented in a global sense so there could be a large gap between real waste quantity and the calculation. The global waste estimation is given by the formula: Global waste = (ratio x global production) - global production.

II.I.3.2. Quality of liquid effluent generated by mining

Every ore, whether metallic or non-metallic, rarely contains one mineral, but is likely to contain a large number of potential pollutants, in addition to the material to be upgraded. Moreover, industrial processing methods use chemical compounds, which may also create pollution. These compounds are present in small quantities and often dissociate fairly rapidly into other molecules. Consequently, analysis of the pollutant potential of the extraction and physical preparation of an ore, whatever its type, must take into account the pollutant potential of each mineral species, including those resulting from the *in situ* weathering of the primary minerals in the ore and its surroundings. This study must naturally consider both the major and trace elements present.

As discussed above, the waste-waters are directly related to the solid wastes because of the drainage from mine workings and waste heaps. In certain mines where ores have high sulfur content, drainage from mine workings and waste heaps can become highly acidic and can contain high concentrations of dissolved heavy metals.

AMD forms when sulfide minerals are exposed to H_2O and O_2, and become oxidised forming acidic, sulfate-rich drainage. There are many types of sulfide minerals: iron sulfides are predominately pyrite and marcasite (FeS_2), but other metals may be complexed with sulfides e.g. chalcopyrite ($CuFeS_2$), covellite (CuS), galena (PbS), sphalerite (ZnS) and arsenopyrite ($AsFeS_2$). Pyrite also commonly occurs with these metal sulfides thereby causing AMD where Cu, Pb, Zn and As are mined.[8]

The metal composition and concentrations in AMD depend on the type and quantity of sulfide minerals present. Some AMD can have a pH = 3 or lower; sulfate levels of 800-1,800 mg/L; and metal levels up to 50 mg/L Cu; 1,000 mg/L Fe; 12 mg/L Pb; 1,700 mg/L Zn; and cadmium levels of several milligrams per litre, depending on the content of the ore.[10] The quality of drainage emanating from underground mines or backfills of surface mines is dependent on the acid-producing (sulfide) and alkaline (carbonate) minerals contained in the disturbed rock. In general, sulfide-rich and carbonate-poor materials produce acidic drainage. Acidity in AMD is comprised of mineral acidity (Fe, Al, Mn, and other metals depending on the specific metal sulfide) and H^+ acidity.[8]

Ore	Ratio	Austria		Finland		France		Germany		Greece		Ireland		Italy		Portugal		Spain		Sweden		U.K.	
		m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.	m.p.	g.w.
Fe	6.2	22144	46345	1867	4110	72373	153431	1647	3280	1300	2756		0		0	138	399	36146	74510	200965	426046	1053	2232
Cu	450			95	42655	2	808	3	1392	1	584	0				969	443926	175	78710	836	375354	4	1706
Zn	32			186	5146	210	6510	169	14524	226	6907	1821	58436	305	9455	1	19	2262	70131	1679	52049	31	961
Pb	32			20	620	11	332	91	2806	238	7418	397	12316	139	4300			523	15222	1001	31031	14	425
Bauxite	3					5738	11596			22823	45646			275	532	22	2138	9	16				
Sn	100						0									11	1068	1	69			30	2940
W	100	11	1060			1	53											1	72	1	109		
Mn (48%)	6									20	100			31	157								
Cr (46%)	2			2765	2751					304	304												
Ni	560			44	24596					161	89887					703	16072						
Ilmenite	25																						
Ag	0					002		010		06				0.15				2.0		2			
Au					13965	0	34770											.002	58806	0084	60895		

Table I.3. Metallic ore production and waste moved in the extraction process (10-year estimation x 10^3 tonnes) (Source: BRGM (2001): *Management of mining, quarrying, and ore-processing waste in the European Union)*

The oxidation of iron disulfides and subsequent conversion in acidity occur through several reactions.[11] The equations show that 1000 tons of rock containing 1%S, all as pyrite, would yield upon complete reaction 31.25 tons of acidity. Therefore, 31.25 tons of 100% $CaCO_3$ would be required to neutralise the acidity generated. If any of the processes represented by the equations were slowed or stopped altogether, the generation of AMD also would slow or cease. Thus removal of air and water from the system, two of the three principal reactants, would stop pyrite from oxidising.[8]

Effluent from tailings ponds may contain in addition concentrations of chromium of several milligrams per litre. The decant water from base metal mining tailings may also contain high concentrations of thiosalts. Finally the presence of chemicals used in flotation and other metal concentration processes could create toxicity problems when released in effluents.

Surface run-off may also pose significant environmental problems through erosion and carry over of tailings and other mining residues. Thus explosives such as ammonium nitrate may be present in surface run-off and transport of mined material and machinery maintenance and repair can also lead to contamination of surface water by oils and other organic compounds.

Since excavation and reworking gives rise to different physicochemical conditions from those prevailing in the *in situ* deposit, the chemistry of the elements concerned must also be considered. Some mineral species are believed to be stable in the natural environment and harmless to man and the environment, apart from possible detriment attributable to the fines fraction. The pollutant potential of this type of ore has to be analysed individually in accordance with the processes employed for their conversion and for their adaptation to the intended use. Ores that fall into this category include aluminium (bauxite), tin (cassiterite), iron, manganese, talc, titanium (rutile or ilmenite), and zirconium. Analysis of the pollutant potential associated with ore processing has to take into account the industrial method(s) used to process the ore to extract the useful components, e.g. flotation, cyaniding, amalgamation.

Minerals	Coal extraction	Ferrous metal extn.	Non-ferrous metal extn	Non-ferrous metal prod.	Industrial Minerals
Ag				X	
Al					X
As	X		X	X	
B				X	
Be				X	
Ca	X		X		
Cd			X	X	
Cr	X		X	X	
Co				X	

Minerals	Coal extraction	Ferrous metal extn.	Non-ferrous metal extn	Non-ferrous metal prod.	Industrial Minerals
Cu			X	X	
Fe		X	X		
Hg			X	X	
K			X		
Mg	X				
Mn					X
Ni				X	
Pb	X		X	X	
Na	X	X	X		
Sb				X	
Se				X	
Si	X				
Tl				X	
V				X	
Zr	X		X	X	
Br			X		
Cl	X	X	X	X	X
F			X	X	
S	X	X	X		
N	X			X	
CN^-	X	X	X	X	
aromatic hydrocarbons	X			X	
aliphatic halogenated hydrocarbons	X			X	
aromatic halogenated hydrocarbons	X			X	
phenols	X	X	X		
sulfides	X		X		

Table I.4. Correlation between industrial activity and pollutants (metals, minerals, organics) (Source: BRGM (2001): Management of mining, quarrying and ore-processing waste in the European Union)

Some metallic elements are considered to be stable in the natural environment e.g. iron, magnesium, and manganese. Most metallic ores exhibit hazardous components (Table I.4).[1]

Ion	Iron ore flotation	Copper sulfide flotation	Lead-Zinc flotation	Other sulfide flotation	Non-sulfide flotation
Al	0.009-5.0	<0.5	-	6.2-7.8	210
Ag	-	<0.1	-	<0.02	0.04
As	-	<0.02-0.07	-	0.02-3.50	<0.01-0.15
Be	-	-	-	<0.002	36
B	-	-	-	<0.01	<0.01-0.65
Ca	55-250	-	-	0.6	43-350
Cd	-	0.05-3.0	1.2-16.4	<0.01-0.74	<0.002-0.01
Co	-	1.68	-	-	-
Cr	-	-	9.8-40	0.03-0.04	0.02-0.35
Fe	<0.02-10.0	550-18800	2900-35000	<0.5-2800	0.06-500
Hg	-	0.0006-0.006	-	0.0008-27.5	-
K	-	-	-	-	77
Pb	0.045-5.0	<0.01-21	76-560	<0.02-9.8	0.02-0.1
Mg	-	-	-	1.93	320
Mn	0.007-330	31	296-572	0.12-56.5	0.19-49
Mo	-	29.3	-	<0.05-21	0.2-0.5
Na	-	-	-	-	270
Ni	0.01-0.20	2.8	-	0.05-2.4	0.15-1.19
Sb	-	<0.5	-	<0.2-64	-
Se	-	<0.003	-	0.144-0.155	0.06-0.13
SiO_2	-	46.8	-	-	-
Te	-	-	-	<0.08-0.3	<0.2
Ti	-	-	-	-	<0.5-2.08
Tl	-	-	-	-	<0.05
V	-	-	-	<0.5	<0.2-2.0
Zn	0.006-10	4.8-310	160-3000	0.02-76.9	<0.02-19
Rare earths	-	-	-	-	4.9
Chloride	0.35-180	-	-	1.5	57-170
Fluoride	-	-	-	4.8-11.7	1.3-365

Ion	Iron ore flotation	Copper sulfide flotation	Lead-Zinc flotation	Other sulfide flotation	Non-sulfide flotation
Nitrate	-	-	-	-	1.25
Phosphate	-	20.8	-	-	0.8
Sulfate	5-475	-	-	-	9-10600
Cyanide	0.008-0.02	<0.01-0.17	-	<0.01-0.45	<0.01
Sulphide	-	-	-	<0.5	<0.5
NH_3	-	-	-	-	1.4

Table I.5. Concentrations of elements (mg/L) in effluents from flotation circuits
(Source: R. W. Smith, *Liquid and Solid Wastes from Mineral Processing Plants*,
Mineral Processing and Extractive Metallurgy Review **16**, 1-22, (1996))

Until now attention has been concentrated on liquid effluents from mine or tailings drainage or seepage but particularly important are the liquid effluents arising from processing plants. Many different waste substances, both toxic and non-toxic, can be potentially discharged from mineral processing concentrators. Thus in flotation plants, a number of reagents are added at various stages of the processes to effect the separation. Among these are collectors, non-ionic extenders, frothers, organic and inorganic activators and depressants, dispersing agents, and flocculating agents and potentially they can remain in the waste solutions ultimately discharged from the plants. Actual ranges of measured quantities of various substances discharged from flotation plants are listed in Table I.5 and various other reported physicochemical characteristics of such waters are listed in Table I.6.[12]

Property	Iron ore flotation	Copper sulfide flotation	Lead-Zinc flotation	Other sulfide flotation	Non-sulfide flotation
Conductivity (μω)	130-375	-	-	-	650-17000
Total dissolved solids (mg/L)	0.3-1090	395-4300	-	68-2600	192-18400
Total suspended solids (mg/L)	0.4-1900	114000-465000	20500-269000	2-550000	4-360000
COD (mg/L)	0.2-36	-	-	15.9-238	<1.6-39.7
Total Organic Carbon (mg/L)	-	-	-	7.8-290	9-3100
Oil and grease (mg/L)	0.03-90	<0.05-10	-	2.0-11.4	<1-3.4
pH	5-10.5	8.1-10.1	7.9-11	6.5-11	5-11

Table I.6. Physicochemical characteristics of effluents from flotation circuits
(Source: R. W. Smith, *Liquid and Solid Wastes from Mineral Processing Plants*,
Mineral Processing and Extractive Metallurgy Review **16**, 1-22, (1996))

References to Chapter II.I

1. BRGM (2001): *Management of mining, quarrying and ore-processing waste in the European Union*, 79 pp., 7 figs., 17 tables, 7 annexes, 1 CD-ROM (Collected data)
2. C N Alpers, D K Nordstrom and J M Burchard, *Compilation and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California, 1940-1991*, USGS Water Resours. Inv. Rep. 91-4160, 173 pp, (1992)
3. D Banks, P L Younger, R T Arnesen, E R Iversen and S B Banks, *Mine-water chemistry: the good, the bad and the ugly*, Environm. Geol. **32**, 157-174, (1997)
4. G C Miller, *The environmental issues in mining.* In Mining Environmental Handbook: effects of mining on the environment and American environmental controls on mining. J Marcus (Ed), Imperial College Press, London, 725-726 (1997)
5. R Cidu, C Biagini, L Fanfani, G La Ruffa and I Marras, *Mine closure at Monteponi (Italy): effect of the cessation of dewatering on the qualità of shallow groundwater* Applied Geochemistry, **16**, 489-502, (2001)
6. Abandoned Mine Site Characterization and Cleanup Handbook, EPA 530-C-01-001, March 2001
7. N Kuyucak, *Mining, the Environment, and the Treatment of Mining Effluents,* Int. J. Environ. Pollution **10**(29), 315-325, (1998)
8. J G Skousen, A Sexstone and P F Ziemkiewicz, *Acid Mine Drainage Control and Treatment,* in Reclamation of Drastically Disturbed Land, Agronomy Monograph no. 41, R I Barnhisel et al. (ed.), ASA, CSSA, and SSSA, Madison, WI, p. 131-168, (2000)
9. C Di Nucci, M Pelino, A Russo Spena and F Vegliò, *The effects of amd, acid mine drainage, arising from the campiano mine: soil and water remediation*10. BOSICON, International Conference on the Remediation of Polluted Sites, Rome (2006)
10. World Bank, *Pollution Prevention and Abatement: Base Metal and Iron Ore Mining*, Draft Technical Background Document, Environment Department Washington, (1998)
11. G Geidel and F T Caruccio, *Geochemical factors affecting cola mine drainage quality*, in Reclamation of Drastically Disturbed Land, Agronomy Monograph no. 41, R I Barnhisel et al. (ed.), ASA, CSSA, and SSSA, Madison, WI, p. 105-130, (2000)
12. R. W. Smith, *Liquid and Solid Wastes from Mineral Processing Plants*, Mineral Processing and Extractive Metallurgy Review **16**, 1-22, (1996)

II.

CHAPTER II.II: METALLURGY

II.II.1. INTRODUCTION

Metal production begins with mining of ores, and then the ores are refined or smelted. The raw material, cast into ingots, may be then sent to basic metal fabricators for further processing.

During the last 20 years, regulation of water disposal from metalworking operations has become more and more rigorous. Previously water treatment mostly involved end-of-pipe treatment, where the total discharges from a facility were treated without regard to the source of the water within the facility. Conventional treatment involved chemical/physical processes where soluble components were first chemically precipitated, and the resulting colloidal components, together with any other suspended contaminants, were flocculated. The water would then be passed into a clarifier, where the sludge was removed and pumped through a filter press for dewatering and the clarified water discharged. The system was expensive to operate, since labour requirements and chemical and disposal costs were high.

First, and most importantly, "end-of-pipe" treatment has largely been replaced by point-source treatment allowing removal of contamination from heavily loaded effluents with several small treatment systems carrying out the operation required by the whole facility, resulting in more cost-effective procedures[1].

II.II.2. METAL PRODUCTION AND PRIMARY FABRICATION

The sequence of processes involved in transforming an ore into a finished metal product includes:

- preparation and concentration of the ore,
- conversion of the ore into pure metal by pyro- or hydro-metallurgical processes,
- melting the metal,
- preparing the moulds for castings,
- casting,
- finishing.

These various processes and the nature and composition of the effluents generated will be considered below.

Following mining and upgrading of the metal-containing ore the resulting concentrates are smelted to release the metal in an elemental form. The composition of the raw material determines the choice of smelting process, thus sulfidic ores are mainly treated by pyrometallurgy whereas oxidic, and complex ores tend to follow a hydrometallurgical route. In addition in some examples a combined process involving for example, pyrometallurgical roasting followed by hydrometallurgical leaching, solution purification and metal recovery.

II.II.2.1. Pyrometallurgy

As the name implies this technology the chemical reactions are carried out at high temperatures. A typical flow sheet would contain some or all of the following operations: roasting, smelting, converting, fuming, refining. The main sources of waste emissions from these processes are: waste gases of various compositions; solid wastes, e.g. slag, dusts; wastes waters from cooling circuits and waste gas scrubbing.

II.II.2.2. Hydrometallurgy

In a hydrometallurgical circuit the concentrated ore is first leached by an aqueous reagent solution and the resulting suspension filtered to remove unreacted solids; the solution containing the metal(s) is then purified to produce a concentrated solution of the desired metal; finally the metal is recovered from solution and refined. This circuit provides many more opportunities for liquid effluents from all stages, as well as solid residues from leaching.

The next sequence of processes, casting, involves turning molten metal into various shapes as determined by the shape of the mould. For these operations the foundries typically use a mixture of recycled scrap metals and metal ingot as a raw material. Hence the first stage in processing involves preparation of the scrap materials, which also may be done by the scrap metal supplier. This consists of cutting the materials to the appropriate size for the furnace, cleaning and degreasing, which can be accomplished with solvents or by burning off any organic contaminants. Prepared scrap metal is weighed and additional metal, alloys, and flux may be added prior to adding the metal to the furnace. This flux removes the impurities forming a molten slag that can be removed from the molten metal. The molten slag is allowed to cool by quenching with water. This provides a stream of polluted waste-water for treatment and disposal.[2]

The molten metal is then cast into ingots or into objects of various desired shapes. These shapes are often produced by pouring the metal into sand-cast moulds from which after cooling the metal casting can be separated. Sand casting techniques can generate substantial volumes of waste sand that may be recycled after the chemical binders in the sand have been removed. In wet sand reclamation, water is used to remove these binders and treatment of the resulting waste-water is needed. Rapid cooling of hot castings by quenching in a water bath is practiced by some foundries and die casters to speed the process and to achieve certain metallurgical properties. The water bath used for this process may be plain water or may contain chemical additives to prevent oxidation.

This text is concerned with the treatment of liquid effluents so that all other solid and gaseous wastes will be disregarded except where they also generate a liquid waste. Thus overall the metallurgical operations that generate liquid, mainly aqueous, effluents include:

Pyrometallurgy:

- wet scrubbing of furnace off gases: discharge and blow-down,
- cooling waters for: process equipment; slag; castings,
- leachate from slag and waste tips,

- sand reclamation,
- washing of castings, etc.,
- cleaning.

Hydrometallurgy:

- leachate from ore/tailings dumps,
- wash waters,
- spent electrolyte baths,
- cooling waters,
- cleaning.

In addition both technologies require energy often produced using steam generation, where boiler ‘blow-down’ is an important source of waste-water, and the generation of waste-waters from spillages and storm water which may be contaminated should not be neglected. The majority of liquid wastes will consist of water and aqueous solutions but some organic compounds may also occur arising from oils and greases used for lubrication.

II.II.3. CHARACTERISTICS OF WASTE-WATERS FROM METALLURGICAL OPERATIONS

In general, the sources of waste-water discharges in metal fabrication plants are process water, cooling water, wet air pollution control equipment, and service plants (such as boilers). In the case of secondary metal production, the aqueous cleaning and rinsing in the scrap preparation have to be included.

Waste-waters from metallurgical operations are likely to contain: inorganic metal compounds, organic compounds, and particulate matter. Process waters, emergency fire water, and chemically contaminated water should be separated and contained to allow easier management and the possibility for reuse within the plant. If it is not possible to treat these on-site they may have to be removed from the premises by a contractor licensed to carry such waste.

Waste-water from high temperature furnace operations mainly consists of non-contact cooling water and wet scrubber effluent. Some foundries using cupola furnaces also generate waste-water containing metals from cooling slag with water[3].

Waste-water generated in certain finishing operations such as quenching and deburring can be high in oil and suspended solids that can be released into process effluents, and treatment is required before discharge. Waste-waters from tumbling operations may contain metals and surfactants.

Foundries, generally do not need large quantities of process water, but can generate more than 20 m^3 of waste-water per tonne of molten metal when cooling water, scrubber water, and process water are not regulated. Untreated waste-waters from these processes may contain high levels of suspended solids, and typically copper (0.9 mg/L), lead (2.5 mg/L), total chromium (2.5 mg/L), hexavalent chromium, nickel (0.25 mg/L), and oil and grease. The characteristics of the waste-water will depend on the type of metal and the quality of scrap used as feed to the process.[4]

II.II.3.1. Discharge and blow-down from wet scrubbers

When a wet scrubber is used to control air pollution, the scrubber effluent becomes a waste-water stream. Air pollutants collected in wet scrubbers include particulate matter, acid gases, volatile organic compounds (VOCs), and some odour-causing compounds. Reduction of air pollution is a cost effective step to minimize this waste-water stream. Particulate matter may be removed by settling and clarification and the resulting sludge dried and landfilled.[1]

Large quantities (up to 13 m^3/minute) of wet scrubber waste-water can be produced in plants using large cupola furnaces. This typically highly alkaline or acidic water may contain metals and before being discharged to the municipal water treatment plant must be neutralised. If amine scrubbers are used, the amine scrubbing solution can be released into the plant effluent system through leaks and spills.[3]

II.II.3.2. Process waste-water

II.II.3.2.1. Aqueous cleaning and rinsing[5]

The first step in metal recycling is preparation of the scrap materials, i.e. cleaning and degreasing. Traditionally, oily parts were cleaned by either washing in solvent or suspending them in a solvent vapour chamber. This typically involved chlorinated solvents, however strict restrictions on their production and use have led to replacement by aqueous and semi-aqueous cleaning reagents. Hence discharges of spent aqueous cleaning solutions and rinse water frequently make up a significant portion of effluents from a typical metal fabrication facility. Factories that switch from solvent cleaners often notice a significant increase in waste-water volume and in some cases, compliance problems. The use of aqueous cleaning solutions, however, generally results in reduction of total disposal costs when compared to solvent cleaning as systems using aqueous cleaning can introduce filtration equipment allowing solutions to be reused, with significant reduction of costs.

II.II.3.2.2. Aqueous and semi-aqueous based cleaners[5]

The use of aqueous and semi-aqueous cleaners has grown tremendously. The technology of these cleaners has improved significantly so that they are now considered as reliable alternatives for many solvent-based applications.

They can be categorized into two major groups: acidic and alkaline-based products, both containing surfactants, emulsifiers, and detergents. Most acidic products contain a blend of different acids depending on the application for which the cleaner was designed. Likewise, alkaline products may contain builders which help in the cleaning process, hard water control agents, rust inhibitors, and corrosion inhibitors to protect soft metals.

Semi-aqueous cleaners are water/solvent based mixtures many containing terpenes, which have a typical odour. Advantages of this type of cleaner over aqueous cleaners include the greater ability to dissolve oil and grease and hold it longer in solution. The disadvantage of this is that the oil and grease is more difficult to remove once it has been emulsified in the solution. These types of products are used quite often in ultrasonic and other agitation devices. Drying of parts may take longer when changing from a solvent-based to an aqueous-based process. Additionally, parts may be more susceptible to rusting due to contact with water and longer drying times.

Prolonging the life of cleaners.

Since discharges of spent aqueous cleaning solutions and rinse water frequently make up a significant portion of the waste-water, methods to reduce, recycle and reuse aqueous solutions have been developed.[5]

II.II.3.2.3. Slag cooling

The removal of impurities from ore concentrates or scrap materials is usually accomplished by adding lime-based flux agents to combine with the impurities and produce a molten slag that can be removed from the molten metal. As the slag cools, it expands and forms a dusty calcium silicate residue which is recognised today as a potential pollutant. Slag cooling and disposal present particular problems. Conventionally the molten slag was poured into a pot, dumped in a disposal yard, and left to cool naturally, perhaps assisted by water spraying. This is a noisy, dusty process with a potential risk of steam explosions. In conjunction with Nippon Steel Corporation, Astec has improved slag cooling and treatment. Molten slag is rapidly cooled on a special steel pan, and transferred to a water pool for secondary cooling. This improves the working environment, increases productivity in the slag treatment area by some 75%, and eliminates the need for primary crushing.[6]

Slag cooling water has no quality requirements, so normal river or ground water can be used. Water consumption can be assumed to be about 0.05-0.01 m^3/t of waste if state-of-the-art slag extractors are used. In the HIsmelt Plant, water for cooling pig iron and slag was used from blow down from gas cleaning scrubber circuits and storm water run off. This recycling of water reduces water usage and results in minimal effluent for disposal.[7]

II.II.3.2.4. Casting Waste-water[3]

Both process waste-water and waste non-contact cooling water may be generated by die casting. Non-contact cooling water will probably have elevated temperature and very little or no chemical contamination. Process waste-water from die casting can be contaminated with oil and phenols from spent die lubricants, hydraulic fluid, and coolants. As with foundries, die casting may also generate waste-water high in oil and suspended solids from finishing operations such as in-process cleaning, quenching and deburring. Typical waste-water treatment will consist of oil/water separation and/or filtration before discharge to a municipal water treatment plant. Facilities generating large volumes of waste-water may also incorporate biological treatment.

II.II.3.2.5. Waste solids leachate

Solid residues from ore beneficiation, concentrate residues and slags can be leached by water especially if as in the case of concentrate leaching some residual leaching solution, such as dilute acid, is present. In addition, the presence of natural bacteria in ore and concentrate residues can stimulate the conversion of sulfide minerals into sulfuric acid thus posing an environmental problem for a considerable time. Therefore such residues should be contained and the any leachate treated before considering discharge into the environment.

II.II.3.2.6. Sand reclamation[8]

Although wet reclamation was used in the 1950s and 1960s, it has been nearly eliminated as a method of sand recovery. In this process water separated the sand from binders by using their different water solubilities. This worked well with clay bonded systems and sodium silicate binders. However now chemical binders are often no longer sufficiently hydrophilic to dissolve in water, and organic resins that do dissolve together with other water soluble impurities can cause significant water contamination. So the high volume of waste-water and strict environmental regulations can make wet sand reclamation too expensive.

II.II.3.2.7. Boiler blow-down

Periodically, suspended and dissolved solids build up in steam boiler systems, and are “blown down” or discharged to the sewer. Several methods can be used to minimize these discharges, thus the first step in reducing boiler blow-down is to minimise steam production. Alternatively deionized water can be used as feed water, when relatively small additions of chemicals are required to control pH and scavenge oxygen (which reduces corrosion). Recycle of boiler blow-down may be possible, if a cooling tower is nearby, by pumping the blow-down to the cooling tower sump, gaining a dual use of the boiler water and substituting the cooling tower blow down for that of the boiler. If the boiler feed water is city water softened by chemicals, then the boiler blow-down may require treatment before discharge. Re-circulation of the treated blow-down to a cooling tower or other process should be investigated[5].

References to Chapter II.II

1. http://www.watertechonline.com
2. EPA Office of Compliance Sector Notebook Project: Profile of the Metal Casting Industry, February 1998
3. http://www.msu.edu/course/eep/255/MetalCastingCase.htm
4. World Bank, *Pollution Prevention and Abatement: Foundries*, Draft Technical Background Document, Environment Department Washington, (1998)
5. Shop Guide to Reduce Wastewater from the Machining and Metal Fabrication Industry, A Competitive Advantage Manual *Prepared by:* Institute of Advanced Manufacturing Sciences *and* Waste Reduction and Technology Transfer Foundation USA, April 1996
6. http://www.borax.com/pioneer12.html
7. www.hismelt.com.au
8. http://www.p2pays.org/ref/01/text/00778/chapter3.htm

II.

CHAPTER II.III: OPTIMUM AND HIGHLY EFFICIENT WASTE-WATER TREATMENT TECHNIQUES

As discussed in Chapters II.I and II.II, process waters from mining and metallurgical operations are widespread throughout the world and can become contaminated by various pollutants. These substances include powders, chemicals such as cyanide, fluoride, sulfide, metal ions, oils, organic and other compounds, sometimes rendering the water useless for recycling as process water, often dangerous for the environment, and sometimes causing losses of valuable materials. Sources of water contamination may be found at mines, mills, off-shore platforms, processing plants, tailing ponds, etc.

Sometimes, due to their chemical complexity and/or volume, these process waters cannot be treated economically even in cases where they contain valuable materials. Smith[4] showed in detail the characteristics of liquid and solid wastes from mineral processing plants. Various techniques and available technologies were discussed and the quality and quantity of typical pollutants listed. In the following discussion the various sources of waste-waters will be considered together with various effective methods of treatment.

II.III.1. CONVENTIONAL TREATMENT

Waste-water streams have traditionally been treated by a combination of physicochemical processes such as flocculation, precipitation, and filtration, and biological treatment such as activated sludge and biofilm processes. Such treatments are usually effective in reducing organic pollutants to a level suitable for disposal into public sewerage or natural waterways. However, they often fail to reduce the concentration of heavy metals below permissible limits. Further, these technologies usually do not provide the selectivity necessary to create valuable product streams suitable for recycle or re-use, and as a consequence the by-product sludge can itself become a disposal problem.[1]

Thus, current and future technologies in the field of mining and metallurgical waste-water treatment will eventually have to deal with areas such as:

- process water treatment and recycling (reuse),
- removal and/or recovery of ions: heavy and/or precious metals, anions, residual organic chemicals, complexes or chelates,
- cyanide and arsenic emission control, recovery or destruction,
- separation of oil spills, including the recovery of solvent extraction liquors,
- acid mine waters containing considerable amounts of harmful base metals such as nickel, copper, zinc, lead, in addition to ferrous iron and sulfate,
- control and removal of residual chemical reagents such as frothers, flotation collectors and modifiers, activators or depressing agents, pH regulators.

The processes based on the use of chemical reagents are usually referred to as *"conventional"* technologies. The conventional process for treating liquid effluents containing metals ions is precipitation-aggregation (coagulation/flocculation)-settling as hydroxides or insoluble salts.[2] However, this method, from a technical point of view, presents certain limitations, as will be discussed later.

Waste-water treatment systems may be classified by the type of unit operation or process or by the principal removal function performed. To facilitate a general comparison of the various operations and processes, information is presented in Table III.1 on: the principal contaminant to be removed; the source of waste-water and the types of operations or processes that can be used for purification. In Figure III.1 the different ranges of concentration of the contaminants over which the available technologies are effective are presented.

Following the treatment of two of the major sources of environmental concern are described: mine waters and tailing ponds, followed by discussion of the most common methods of treating waste-water streams from these industries: precipitation and chemical oxidation.

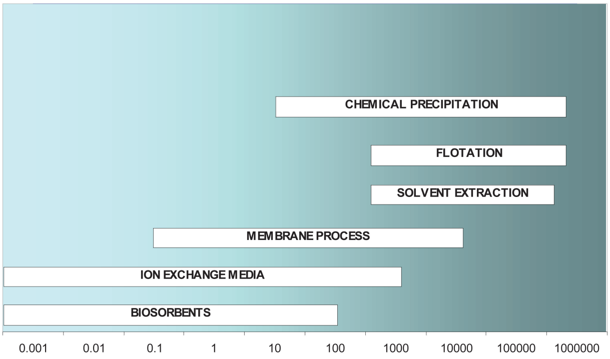


Figure III.1. Waste-water treatments applicable to different ranges of solute concentration

II.III.1.1. Mine waters and drainage

Treatment necessary to remove contamination of mine water depends upon its chemistry. Thus:

- if the mine water contains an excess of alkalinity, it will probably be amenable to treatment by simple aeration to remove the dissolved iron, generally the major contaminant. Beneficial correction of other contaminants is also likely to occur during this process. Suspended particles generated following aeration are detained in purpose designed sedimentation ponds; if the mine water contains an excess of acidity, it will require the addition of alkali. The acidity is neutralised allowing the conversion of dissolved contaminants into suspended particles which are then detained in sedimentation ponds,
- for low flows of acidic mine water, passive treatment may be possible by the use of ‘low cost’ materials such as composts and limestone. Bacteriological and chemical processes can generate alkalinity that allows sedimentation of generated solids. These operations require little manual intervention and minimise on-going treatment cost. This form of treatment may be appropriate for incorporation into restoration schemes for mining sites,
- most mine water treatment schemes incorporate wetlands technology to provide tertiary treatment to ensure that the mine water meets the standards required by legislation.

Elements	Sources of waste-water	Processes[3]
Arsenic	metal pickling and cleaning; copper smelter, refiner and metal salt production; lead/zinc ISP smelter	*Arsenic* cannot be treated to the regulated levels by pH adjustment and precipitation. It is most often treated by *precipitating as ferric arsenate or the sulfide*. Arsenate can also be polished to low levels, <10 µg/L with *activated alumina or a cation resin*, which has been exchanged with ferric ion. Currently normal commercial *ion exchange* resins are ineffective at removing arsenic.
Barium	metallurgical industry	*Barium* is removed from solution by *precipitation* as barium sulfate. *Coagulation* of barium sulfate is capable of reducing barium to effluent levels of 0.5 mg/L. Barium can also be removed from solution by *ion exchange* and *electrodialysis*, although these processes would be more expensive than chemical precipitation.
Cadmium	cadmium processing, solder cleaning operations; copper smelter and metal salt production	*Cadmium* cannot be precipitated to the regulatory levels by pH adjustment alone. However carbonate, phosphate, and sulfide, precipitates are all very insoluble. It can also be removed very effectively with chelating ion exchange resins.
Nickel	metal treatment and finishing; aluminium and steel production; ore beneficiation	*Nickel* that is not complexed or chelated can be precipitated as nickel hydroxide. Complexed nickel must be treated with sulfide. The precipitation of nickel phosphate is effective for lightly complexed nickel. Nickel can be removed with cation and chelating resins.
Lead	copper smelter, metal salt production and products from refined copper; lead/zinc ISP smelter, electrolytic zinc and lead production, metal processing plant; acid mine drainage	*Lead* is often treated by precipitating lead sulfide or phosphate. It can also be treated by ion exchange or by reduction, i.e. by media filtration in the presence of agents that reduce soluble lead cations to insoluble lead atoms.
Zinc	electrolytic zinc and lead production, metal processing plant; AMD	*Zinc* can be precipitated as the hydroxide, carbonate, phosphate, or sulfide. It can also be removed by ion exchange.
Copper	copper smelter, refining, metal finishing, wire drawing; AMD	*Copper* can be removed from waste-water by precipitation of the insoluble hydroxide. Also removed by precipitation as metallic copper and ion exchange.
Chromium	pickling operations	*Chromium,* usually found in the form of dichromate anion, and, following reduction to Cr^{3+} can be precipitated as the hydroxide or, as the phosphate or sulfide. It can also be removed by both cation and anion resins.
Silver	pickling operations	*Silver* can be reduced to less than 0.1 mg/L by phosphate precipitation, but to go to lower concentrations sulfide precipitation is necessary. It can be reduced to metallic silver with weak reducing agents. Silver can also be removed by media filtration in a reducing environment and by sulfide based ion exchange resins.

Elements	Sources of waste-water	Processes[3]
Iron	copper smelter, refining production; pickling, steel mills, foundries, chemical milling, wire drawing; AMD	*Iron*, both ferrous and ferric can be precipitated to low concentrations by pH adjustment, carbonate, phosphate, and sulfide precipitation.
Mercury	industrial waste-waters originated from NaCl electrolysis using the Hg method	*Mercury* can be precipitated to low levels using carbonate, phosphate, or sulfide after oxidation. It can also be removed by ion exchange. An oxidation step is required ahead of the ion exchange column and either a chelating resin or a mercury selective resin should be used.
Selenium	*Selenium* may be present in metallic sulfide ores	The selenious, Se(III), ion appears to be the most common form of selenium in waste-water. Selenium can be removed from waste-waters by precipitation as the sulfide at a pH 6.6. Effluent levels of 0.05 mg/L are reported.
Cyanide	gold ore processing	*Cyanide,* oxidizable cyanides can be treated by chlorine dioxide, hydrogen peroxide or other oxidants. Oxidation should be considered when levels of oxidizable cyanide are too high to be processed by a biological treatment system. There are various alternative methods available for the treatment such as adsorption, ion exchange, and electrodialysis.
Fluoride	metal finishing; aluminium and steel production; ore beneficiation	*Fluoride* is most commonly treated by precipitation as calcium fluoride. If the water is treated with aluminium hydroxide, the fluoride can be reduced to 5 mg/L.
Sulfide	Acid mine drainage	*Sulfide* is treated by chemical oxidation followed by filtration of sulfate salts
Oils	metal-working industries	*Oils* are subjected to primary treatment to separate the oil, and secondary treatments such as flotation.

Table III.1. Waste-water treatment options for various pollutants

II.III.1.2. Tailing pond treatment[4]

So far tailing ponds have been considered as just a method of tailing containment and disposal, but the use of tailing ponds also is the most common type of treatment for waste-waters from mineral beneficiation. A primary function of the tailing ponds is to remove suspended solids. For such purposes it must be properly designed to provide sufficient surface area, retention time, and quiescent conditions. Oxidation and destruction of some noxious substances can also be provided in a properly designed pond. Retention time in the pond can vary greatly depending on climatic conditions, sizes of solids present, etc. Water may leave the pond in a number of ways, including simple overflow; seepage through or under the dam; evaporation, and pumping and recycling to the mill. Zero discharge from the pond can be achieved, in principal, by either chemical treatment and recycling of all the water or, if the environment is sufficiently dry, evaporation from the pond. A primary problem, unless the bottom of the pond is sealed by natural or artificial means, can be seepage into aquifers used by cities or agriculture. Low cost and often used as the only means of removing suspended solids make such ponds indispensable in many mineral industry operations. Settling ponds rather than tailing ponds may sometimes be used if solid concentrations are low and a major quantity of water is to be recycled.

II.III.1.3. Precipitation

II.III.1.3.1. Lime neutralization

In the lime neutralization process, acids are neutralized and metals, such as Fe, Zn, Cu, Al, and Pb, precipitated in the form of metal hydroxides. The mixture of gypsum ($CaSO_4$) and metal hydroxides is called a sludge. The principal reaction can be expressed as follows:

$$Ca(OH)_2 + M^{2+}/M^{3+} + H_2SO_4 \rightarrow M(OH)_2/M(OH)_3 + CaSO_4 + H_2O$$

Air is frequently used to oxidize ferrous to ferric iron during precipitation, because ferric iron sludge is chemically more stable than ferrous iron sludge. The sludge produced is allowed to settle in clarifiers/thickeners. When the solid content of the waste-water is less than 1mg/L, sand-bed filters are employed for polishing, to meet the required level of suspended solids in the final effluent. The supernatant is then discharged to the receiving stream, and the settled sludge is disposed of in specifically designed ponds. Depending on site factors, lime neutralization facilities can vary greatly in degrees of sophistication.[5]

Many small plants have a total daily volume of waste of less than 115 m^3/d and the most economical system for such plants is a batch treatment in which two tanks are provided, each with a capacity of one day's flow. One tank undergoes treatment while the other is filling. Accumulated sludge is either drawn off and hauled to disposal or dewatered on sand drying beds. A spreadable dry cake can be obtained after 48 hours on a sand bed. When the daily volume of waste exceeds 115-150 m^3, batch treatment is usually not feasible because of the large tankage required. Hence a continuous treatment plant is used requiring a tank for acidification and reduction; then a mixing tank, for lime addition; and finally a settling tank. The retention time in the reduction tank is dependent on the pH employed but should be at least 4 times the theoretical time for complete reduction. Twenty minutes will usually be adequate for flocculation. Final settling should have a maximum overflow rate of 20 $m^3/(d\ m^2)$.[3] Continuous lime neutralization facilities range from the simple addition of lime to the tailings pipelines to, in the case of high density sludge process, plants consisting of reactors, clarifiers, and sludge dewatering equipment. The sludge densities vary from 1-30% solids, depending on the metal concentration of the water and the sophistication of the treatment process. Because formation of a voluminous sludge is undesirable, the process parameters (rate of neutralization, oxidation, etc.) are optimised to obtain a dense sludge. The current state-of-art lime neutralization for treating AMD and other acidic waters is called the high density sludge (HDS) process and is capable of producing a more compacted sludge than the traditional method of neutralization.[6]

As discussed above it is impossible to achieve maximum removal for all the heavy metals at a specific solution pH. As seen from Table III.2 lime precipitation is limited in applicability, owing to high solubilities and amphoteric properties of the metal hydroxides. For example lime precipitation could not reduce the Mn^{2+} and Cd^{2+} concentration to the prescribed discharge standards of 0.1 ppm Mn^{2+} and 0.001-0.002 ppm Cd^{2+}.

element/pH	1.65	4.40	5.70	6.90	8.10	9.10	10.1	11.15	12.50
Al	249	168	139	3.40	0.267	0.0924	2.59	5.94	2.55
Ba	0.0749	0.058	0.0441	0.0341	0.0281	0.0224	0.0216	0.0201	0.0100
Ca	300	557	641	720	823	875	915	989	466
Cr	4.85	4.58	2.91	0.0055	0.0001	0.000	0.000	0.000	0.000
Cu	1.80	1.77	1.04	0.0302	0.0071	0.0051	0.0051	0.0050	0.0051
Fe	942	926	578	332	42.1	25.2	10.2	8.00	4.00
Mg	359	354	352	349	346	343	143	6.48	0.547
Mn	113	111	106	98.8	49.5	15.7	2.60	2.23	1.11
Ni	5.75	5.40	5.03	2.37	0.0907	0.0661	0.0587	0.0545	0.0525
Pb	0.349	0.068	0.0229	0.0050	0.0014	0.000	0.0010	0.0126	0.125
Si	23.8	22.7	6.36	4.27	0.919	0.456	0.241	0.0954	0.325
Sr	1.77	1.72	1.39	1.20	1.06	1.02	1.02	1.02	1.01
Ti	3.55	0.264	0.0306	0.0189	0.0050	0.0010	0.000	0.000	0.000
Zn	10.1	8.65	5.67	0.544	0.0001	0.000	0.000	0.0010	0.0124
Zr	0.0919	0.079	0.0700	0.0700	0.0700	0.0700	0.0700	0.0700	0.0700
Cd	0.260	0.255	0.241	0.220	0.160	0.0877	0.0800	0.090	0.108
Co	1.94	1.85	1.80	1.05	0.062	0.0041	0.000	0.000	0.000
F	431	257	141	101	44.0	38.5	28.3	10.7	0.506
Cl	954	825	673	568	478	452	451	448	448
Br	280	277	267	260	258	253	214	213	213
SO_4^{2-}	6305	4830	4329	3425	3353	3211	3185	3158	1381
PO_4^{3-}	337	285	185	28.5	0.0005	0.000	0.000	0.000	0.000

*The oxidation states of the metal ions are not indicated. Species of the same metal with different oxidation states can co-exist but the compositions of such mixtures are difficult to determine beforehand.

Table III.2. variation of cation and anion concentrations (mg/L) with pH.
(Source: D Feng, C Aldrich and H Tan, *Treatment of acid mine water by use of heavy metal precipitation and ion exchange*, Minerals Engineering, **13**(6), 623-642, (2000))

As indicated in Table III.2, calcium and sulfate concentrations decreased as the precipitation proceeded. It is possible that calcium sulfate precipitated from the saturated solution with the hydroxides thus acts as crystallization seeds and co-precipitates. Similarly barium was precipitated as barium sulfate, and silica as calcium silicate. The decrease in the phosphate could be attributed to the formation of low solubility calcium phosphate precipitates. The decrease in the chloride concentration could probably be ascribed to the formation of silver chloride and some other metal chloride complexes. The bromide concentration decreases only slightly, possibly by some adsorption on the hydroxide flocs, while the fluoride formed calcium fluoride precipitates. Iron could not be precipitated completely, owing to the high solubility of ferrous hydroxide. Chemical oxidants are often added at the beginning of the precipitation process to oxidise ferrous iron and divalent manganese.[6]

II.III.1.3.2. Alternatives to lime neutralization

Limestone can remove acidity and precipitate iron and, under controlled condition, higher density sludge can be obtained using $CaCO_3$ instead of lime. However the removal of metals which require a pH >6.5 cannot be achieved, so a combined limestone-lime treatment process has been suggested. The Dowa Mining Co., Japan, uses limestone neutralization to remove iron following biological conversion of ferrous into ferric iron.[5]

Calcium carbonate, the main advantage over lime is its lower price and the production of a denser sludge. However it requires a longer reaction time to treat acid water. Although the process could be accelerated by use of fluidised bed reactors this method is relatively expensive.[6]

Sulfide precipitation with Na_2S, NaHS, FeS, $(NH_4)_2S$, or CaS is more effective for the treatment of waste-waters containing highly toxic heavy metals. The advantages of the sulfide precipitation are the attainment of a high degree of metal removal over a broad pH range, effective precipitation of certain metals even at low pH values, and short reaction time. The drawback is that sulfide precipitation has a tendency to form toxic H_2S at low pH values. The mine water occurring in the Leisvall mine of Boliden Mineral AB, Sweden has been treated with Na_2S to remove low levels of Pb (0.5 mg/L) and Zn (0.7 mg/L).[5]

Ammonia has been suggested to be a feasible alternative to lime for neutralizing low flows containing low acidity.

Magnesium hydroxide can result in a lower volume and denser metal hydroxide sludge, but the rate of neutralization is slow and the maximum reachable pH is 9. $Mg(OH)_2$ is usually employed in treatment plants, such as Canadian Copper Refinery (CCR) in East Montreal, where the disposal cost of sludge is high, in order to reduce sludge disposal costs.[5]

Soda ash (Na_2CO_3) is generally used in remote areas to treat AMD with low flow and low amounts of acidity and metals. Selection of soda ash for treating AMD is usually based on convenience rather than chemical cost. Soda ash comes as solid briquettes and is gravity fed into water by the use of bins or barrels. This system offers less control of the amount of chemical used.

Caustic soda (NaOH) is often used in the remote locations, and to treat waste-waters with low flow and high acidity. It is commonly the chemical of choice if Mn concentrations in the AMD are high.

Caustic is very soluble in water, disperses rapidly, and raises the pH of the water quickly. The main drawbacks are high cost and danger in handling.[7]

II.III.1.3.3. Sector concerned, state of development and level of industrialization

Precipitation is used to remove heavy metals from waste-waters generally as the hydroxide through the addition of lime or caustic to a pH of minimum solubility. Treatment with lime requires a short reaction period, owing to its high solubility (0.15%). However, since the minimum solubilities for the different metals usually found in the polluted water occur at different pH values and several of the hydroxide precipitates are amphoteric in nature, maximum removal efficiency of mixed metals cannot be achieved at a single precipitation pH value. Thus the solubility of chromium and zinc are a minimum at pH 7.5 and 10.2, respectively, and show a significant increase in concentration above these pH values.[3] For this reason, as in the recently developed Savmin process, acid mine water has to be treated in multiple stages. This process involves five stages of heavy metal and magnesium precipitation, gypsum de-supersaturation, ettringite precipitation for the removal of calcium and sulfate, carbonation and recycling of aluminium hydroxide. Precipitation is followed by multistage precipitate-liquid separation, which is slow.[6]

When treating industrial waste-waters containing metals, it is frequently necessary to pre-treat them to remove substances that interfere with the precipitation. For example cyanide and ammonia form complexes with many metals that limit the removal achievable by precipitation. Cyanide can be removed by alkaline chlorination or other processes such as catalytic oxidation on carbon. Cyanide waste-waters containing nickel or silver are difficult to treat by alkaline chlorination because of the slow reaction rate of these metal complexes. Ferro-cyanide $[Fe(CN)_6]^{4-}$ is oxidized to ferro-cyanide $[Fe(CN)_6]^{3-}$ which resists further oxidation. Ammonia can be removed by stripping, break-point chlorination, or other suitable methods prior to the removal of metals.

Heavy metals may also be precipitated as the sulfide and in some cases as the carbonate, as in the case of lead. For many metals such as arsenic and cadmium, co-precipitation with iron or aluminium is highly effective for removal to low residual levels[3].

II.III.1.3.4. Advantages and drawbacks

Lime precipitation is a relatively low cost method of treatment and it is efficient for the treatment of common heavy metals. Traditionally, acid mine water is neutralised in this way, resulting in the concomitant precipitation of iron, aluminium and other metal hydroxides. Treatment with lime requires a short reaction period; however, such neutralisation/precipitation processes may have some drawbacks such as poor quality of the final effluent and the need to dispose of a large volume of sludge.

Conventional methods like precipitation are unfavourable especially when dealing with large volumes of solution which contains heavy metal ions in low concentration. Typically these ions are precipitated as hydrated metal oxides or hydroxides using calcium oxide, sulfides, or xanthiogenates. Precipitation is accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions. For example, industrial waste-waters containing 0.1 g/L of Cu(II), Cd(II) or Hg(II) compounds give respectively 10-, 9- and 5-times larger amounts of sediments; and 6 kg of sediments are obtained from one kilogram of chromates. Precipitation of heavy metals in the form of colloids or amorphous gels and their occurrence as anions, e.g. chromates, as well as the presence of complexing substances (organic and inorganic ligands) in the solutions obstruct this process. For effective precipitation suitable pH conditions and temperature are required and in addition, suitable concentration of metal ions and controlled stirring intensity. Frequently after final filtration, concentration of heavy metal ions in the filtrate still remains at the level of a few mg/L.[8]

This method, from a technical point of view, presents certain limitations, including:

- formation of metal hydroxide is ineffective in dilute metal bearing effluents,
- hydroxo precipitates tends to re-dissolve, depending on the metal,
- pH of minimum solubility of hydroxides is different for the various metals present. For example, the minimum solubility for cupric hydroxide occurs at a pH value around 9.5 while for cadmium hydroxide it occurs at pH around 11,
- precipitation of metals becomes incomplete when complexing or chelating agents are present,
- volumes of sludge formed are large and have a high water content,
- filtration may be difficult as a result of the fineness of the precipitate, and
- treatment by coagulation and settling of effluent with flow-rates of about 2-4 m^3/s is very difficult and costly due to kinetic and scaling problems[2].

These difficulties constitute a great challenge for the modern mining industry.

Where it is possible to remove heavy metals within prescribed limits by precipitation or a combination of precipitation with coagulation/flocculation or filtration the resulting high salinity of the effluent is a problem that limits reuse. Reduction of the concentration of dissolved salts to an acceptable level is an addition requirement and this should be achieved without undue cost. Existing technologies for the removal of salt include among others: evaporation, reverse osmosis, electrodialysis, and ion exchange.[6]

II.III.1.3.5 Economic data[7]

The costs of a technology are divided into: installation (capital) costs and variable operating costs. Installation costs include piping, system foundation, site preparation, equipment, hardware, and labour. Variable costs include cost of reagents, annual labour, and maintenance, including cost of repairs and energy.

As an example, the results of a study carried out by West Virginia University on acid mine drainage treatment, is presented below. This study deals with AMD treatment by neutralization/precipitation based on a 5 year operation period. The amount of reagents was computed using acid neutralization formulae presented by Skousen and Ziemkiewicz (1996).

Annual labour was estimated as the man-hours to run the system for 1 year at a cost of 27 $/h. Other variable costs include repair costs and electricity.

The net present value (NPV) is the value of the total treatment system, plus annual operating and chemical expenses over the specified duration of treatment. A dollar devaluation rate of 6% per annum, for future years of the treatment period, was applied. The annual cost was obtained by converting the total system cost, NPV, to an equivalent.

Costs have been estimated for hydrated lime as neutraliser under three sets of flow and acid concentration conditions (Table III.3).

Flow, L/min Acidity, mg/L	189 100	3780 100	3780 2500
Reagent costs	814	9768	244200
Repair costs	100	3100	10500
Annual labour	6500	11232	11232
Electricity	3500	11000	11000
Installation costs	58400	102000	200000
Salvage value	5750	6500	25000
Net present value	94120	228310	313970
Annual cost	22344	54200	311932

Table III.3. Estimation of costs, in dollars, of treating AMD by neutralisation/ precipitation

Hydrated lime treatment systems have higher installation costs compared with other neutralisers because of the need to construct a lime treatment plant and install a pond aerator. However the cost of $Ca(OH)_2$ is very low. The combination of high installation cost and low reagent cost make $Ca(OH)_2$ systems particularly appropriate for long-term treatment of high flow/high acid situations.

II.III.1.4. Chemical Oxidation

The chemical oxidants in wide use today are chlorine, ozone, and hydrogen peroxide. Their historical use, particularly for chlorine and ozone, has been in the disinfection of water and waste-waters. They are, however, receiving increased consideration for removing from waste-waters organic materials that are resistant to biological, cyanide, arsenic, and other treatment processes.

II.III.1.4.1. Ozone[9]

Ozone is a powerful oxidizing agent that reacts rapidly with many compounds present in waste-waters. It has a relatively low solubility in water, under standard conditions of temperature and pressure, and is unstable, with a half-life of a few minutes. Ozone must therefore be generated on-site. Ozone is effective in many applications from colour and odour removal, to iron and manganese removal and for the oxidation of many complex organic compounds including cyanide and organo-metallic complexes. With the latter the metal ion is released and can be removed by precipitation.

II.III.1.4.2. Chlorine[9]

Chlorine, and in its more readily storable form, the hypochlorite ion, or bleach, is a well-known chemical oxidant and has long been used to purify water and oxidize chemicals in aqueous solutions. The destruction of cyanide and phenols by chlorine oxidation is well-known in waste treatment technology. Recent developments in the use of chlorine oxidation for waste-water treatment are characterized by a greater understanding and control of chlorine oxidation chemistry.

In reactions with inorganic materials terminal end products usually result while organic oxidations usually produce chlorinated hydrocarbons which constitute their own pollution problems.

Alkaline chlorination oxidizes cyanide by the addition of chlorine. The initial reaction forms cyanogen chloride ($CNCl$); this reaction is instantaneous at all pH levels. In the presence of caustic, sodium cyanate is formed from the cyanogen chloride. Cyanide waste treatment can be accomplished in either batch- or continuous-treatment systems. The batch-treatment system is similar to that described for precipitation except that only a small volume needs to be provided for the precipitation of heavy metal sludge and usually it is only necessary to remove sludge at infrequent intervals. In the continuous-treatment systems the oxidation-reduction potential can be monitored and used to control the addition of chlorine. In the presence of excess chlorine, complete oxidation is assured if the pH and retention time are maintained at their proper levels.

II.III.1.4.3. Hydrogen peroxide

While H_2O_2 will oxidize free cyanide, it is common to catalyse the reaction with a transition metal such as soluble copper, vanadium, tungsten, or silver in concentrations of 5-50 mg/L. This simple system is adequate for treating both free cyanide and some weak acid dissociable cyanides such as those complexes with zinc, copper, or cadmium. Less reactive cyanides such as those complexed with nickel or silver may require the addition of a chelating agent to encourage dissociation. Inert cyanides such as ferricyanide can only be decomposed by photo-activation. As with alkaline chlorination, the product of H_2O_2 reaction is cyanate (CNO^-) which is 1000 times less toxic than cyanide, and is often acceptable for discharge. Alternatively, cyanate can be destroyed through acid hydrolysis, forming carbon dioxide and ammonia.

A process using H_2O_2 to remove all forms of cyanides and heavy metals[10] has been developed. In the first step, H_2O_2 and sodium thiosulfate are reacted with free and weakly complexed cyanides to yield thiocyanate. Next, steryldimethylbenzyl-ammonium chloride is added to precipitate ferrocyanide. Finally, ferric sulfate is added as a sweep floc to precipitate other heavy metals. The solids are removed by filtration.

Chemical oxidation has a proven record for cyanide and sulfide removal in the treatment of effluent from mines.

II.III.1.4.4. Cyanide destruction by natural degradation[5]

The widely used method for removal of cyanides and ammonia is natural degradation in holding ponds. Cyanides are biologically or chemically oxidized and are then converted into ammonia and carbon dioxide. Natural degradation of ammonia involves the evaporation of dissolved ammonia gas from the waste-water. Removal is enhanced by increasing the pond area, increasing the pH, and allowing more contact with air. A biological process unique to Homestake Mining in South Dakota decomposes metal cyanide complexes and efficiently oxidizes cyanides to ammonia, which is further oxidized by bacteria (nitrification) to nitrate. Base metal cyanide complexes are selectively oxidized to cyanates by a mixture of SO_2 and air, in the presence of copper as a catalyst in a controlled pH range. This is a proven process and is known as the Inco Method.

A number of operations use hydrogen peroxide to oxidize cyanides to cyanates. Hemlo Gold (Noranda) adds the premixed $CuSO_4/FeSO_4$ reagent to the mill solution, in which the pH is controlled at 9.5 and cyanide is removed with cuprous ions. Other methods such as air stripping, steam stripping, alkaline chlorination with hypochlorite at pH 10-11, engineered wetlands, acidification/volatilisation, adsorbents, and ion exchange resins for the removal of cyanides and ammonia, have limited use.

In addition to the methods normally used for the destruction of cyanide in waste-waters, there exists another group of techniques in which cyanide is regenerated (see below: emerging techniques).

II.III.2. COMBINATION OF DIFFERENT METHODS OF TREATMENT

Often, combinations of unit operations and processes are used to remove other constituents that are not reduced significantly by secondary treatment. Waste-water treatment systems that involve a combination of different operation and processes are usually referred to as “advanced” technologies.

To enhance the lime neutralization process, alternatives to lime as neutralizer could be employed and often more sophisticated solid/liquid separation techniques or general combined techniques are utilized. Thus oxidation or reducing processes could precede or follow precipitation as in the case of removal of iron, chromium, or cyanide. Coagulation, flocculation, and filtration are unit operations often combined with precipitation. In addition, dewatering, metal recovery, or stabilization of the sludge could also follow the precipitation process.

II.III.2.1. Reduction-precipitation

For treatment of chromium wastes hexavalent chromium must first be reduced to the trivalent state, Cr^{3+}, and then precipitated with lime. This is referred to as a reduction/ precipitation process. The reducing agents commonly used for chromium wastes are ferrous sulfate, sodium meta-bisulfite, or sulfur dioxide. Ferrous sulfate and sodium meta-bisulfite may be fed either dry or in solution, and SO_2 is diffused into the system directly from gas cylinders. Since the reduction of chromium is most effective at acidic pH values, a reducing agent with acidic properties is desirable.

II.III.2.2. Precipitation-filtration

More sophisticated solid/liquid separation equipment, e.g. sand filters, are used to meet the stringent final effluent limits on suspended solids arising from the precipitation of metals. When only using precipitation and clarification, the effluent concentration of metals may be as high as 1-2 mg/L. Filtration should reduce these concentrations to 0.5 mg/L or less. Dynasand filters were installed to separate solids and produce a final effluent with turbidity and concentrations below 0.1 mg/L for the heavy metals Zn, Pb, Mn, and Cd.

II.III.2.3. Precipitation-coagulation/flocculation

Following neutralization, the fine precipitate particles in suspension need to be aggregated to improve solid/liquid separation or sedimentation in clarifiers, and dewatering of the sludge for the compaction in basins. Coagulation is a specific type of aggregation, which leads to formation of compact aggregates, called flocs. The addition of a coagulant, such as Al^{3+} and Fe^{3+} salts or organic polymers, helps to discharge or destabilize the electronegative colloids and bridge the neutral particles. The type of polymer, temperature of the system, viscosity, chemical characteristics of the pulp, and external stirring are important parameters in the flocculation process.

II.III.2.4. Precipitation-pH adjustment

When it is necessary to lower the pH to between 6.5 and 8.5 in the final effluent following neutralization at a higher pH, the pH is adjusted to the desired level with either sulfuric acid or CO_2.

II.III.2.5. Precipitation-oxidation

Waste-waters containing cyanide normally are subjected to precipitation for metal ions recovery followed by oxidation for cyanide removal.

II.III.2.6. Oxidation-precipitation

In the above description of lime precipitation it was stated that air is frequently used to oxidize ferrous to ferric ion during precipitation. In some cases an oxidation pre-treatment is carried out. Thus H_2O_2 may be used to oxidize divalent iron and manganese before lime precipitation. A secondary benefit of using H_2O_2 was that oxidation appeared to be effective in destroying some of the taste and odour compounds in the solution. The extent of oxidation was monitored by determination of the ferric concentration.

II.III.2.7. Other technologies

Precipitation-reverse osmosis, precipitation-electrodialysis, and precipitation-ion exchange are "proposed" combinations to remove the problem of the high salinity of the effluent produced by precipitation treatment.

II.III.3. SUMMARY AND CONCLUSIONS

The most widely used methods for treating waste-waters from mining and metal industries are precipitation to remove metal ions and chemical oxidation to remove cyanides often following tailing pond treatments for the removal of suspended solids. Ion exchange is a technique that is still not technically and economically feasible for treating AMD.

In the neutralization/precipitation process, acids are neutralized and metals, such as Fe, Zn, Cu, Al, and Pb, are precipitated in the form of metal oxide/hydroxides. Lime precipitation is a relatively low cost treatment and it is efficient for the treatment of common heavy metals. Traditionally, acid mine water is neutralised by treatment with lime, resulting in concomitant precipitation of iron, aluminium and other metal hydroxides. Treatment with lime only requires a short reaction period, however, this process may have some drawbacks such as poor quality of the final effluent and the need to dispose of a large volume of sludge.

Conventional methods like precipitation are unfavourable especially when dealing with large volumes of solution which contains heavy metal ions in low concentration.

Precipitation may be accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions.

The pH of minimum solubility of hydroxides is different for the various metals thus presenting a problem with multi-element waste-waters. Also the resulting effluent has a high salinity and so limited possibilities for reuse.

The combination of high installation costs and low reagent cost make $Ca(OH)_2$ systems particularly appropriate for long-term treatment of high flow/high acid condition situations.

Often, combinations of unit operations and processes are used to remove other constituents that are not reduced significantly by secondary treatment. Waste-water treatment systems using a combination of different operation and processes are usually referred to as “advanced” technologies.

To enhance the lime neutralization process, alternatives to lime as a neutralizer can be used and often more sophisticated solid/liquid separation techniques or combined techniques are utilized. Thus oxidation or reducing processes could precede or follow precipitation as in the case of removal of iron, chromium, or cyanide. Coagulation, flocculation, and filtration are unit operation often combined with precipitation and dewatering, metal recovery, or stabilization of the sludge could follow the precipitation treatment.

References to Chapter II.III

1. S E Kentish and G W Stevens, *Innovation in separation technology for the recycling and re-use of liquid waste streams,* Chem. Eng. J., **84**, 149-159, (2001)
2. J Rubio, M L Souza and R W Smith, *Overview of flotation as a wastewater treatment technique,* Minerals Eng., **15**, 139-155 (2002)

References to Chapter II.III

3. W W Eckenfelder Jr., Industrial Water Pollution Control, McGraw-Hill, (2001)
4. R W Smith, *Liquid and Solid Wastes from Mineral Processing Plants*, Mineral Processing and Extractive Metallurgy Review **16**, 1-22, (1996)
5. N Kuyucak, *Mining, the Environment, and the Treatment of Mining Effluents,* Int. J. Environ. Pollution **10**(29), 315-325, (1998)
6. D Feng, C Aldrich and H Tan, *Treatment of acid mine water by use of heavy metal precipitation and ion exchange*, Min. Eng., **13**(6), 623-642, (2000)
7. J G Skousen, A Sexstone and P F Ziemkiewicz, *Acid Mine Drainage Control and Treatment,* in Reclamation of Drastically Disturbed Land, Agronomy Monograph no. 41, ASA, CSSA, and SSSA, Madison, WI, p. 131-168, (2000)
8. A Dabrowski, Z Hubicki, P Podkoscielny and E Robens, *Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method*, Chemosphere, **56**, 91-106, (2004)
9. V Cavaseno, Industrial Wastewater and Solid Waste Engineering, Mc Graw-Hill Publication Co. (1980)
10. J E Schiller, *Removal of cyanide and metals from mineral processing wastewater,* U.S. Bureau of Mines Report of Investigation No. 8839, (1983)

II.

CHAPTER II.IV: EMERGING TECHNIQUES AND APPLICATIONS

Over the past 50 years, a wide variety of treatment technologies have been studied, developed, and applied for the removal of contaminants from waters, for example: ion exchange, adsorption, solvent extraction, membrane processes, flotation, electrochemical technologies, biological ion removal, passive methods, and Bauxsol technology.

Of the above new technologies ion exchange, membrane processes and solvent extraction are widely utilised for metal recovery operations. However they are employed for site-specific applications, because these methods are still not technically and economically feasible for treating AMD. Bauxsol technology and some passive methods are receiving increasing interest as alternative to conventional methods for treating AMD, while the others are really 'emerging' ones.

II.IV.1. ION EXCHANGE

(further information on principles, equipment and operation in Section 3).[4]

As discussed above, precipitation processes lose their advantage at low solute feed concentrations. In this instance, an alternative technology is required. The use of a solid matrix for adsorption and ion-exchange of contaminants provides such an alternative. The volume of adsorbent material required increases proportionately with the solute load, so that at higher solute concentrations, equipment size makes such processes economically unfeasible. Applications are typically limited to levels of contaminants in the ppm range.

Synthetic ion-exchange resins have long been used in commercial scale applications for the softening or demineralisation of water. Again, while effective in reducing ionic contaminant levels to low levels, such resins have traditionally suffered from a lack of selectivity. Research has therefore been directed towards improving this selectivity. Experimental and pilot scale research has targeted the use of new ion-exchange resins and zeolite materials for the selective removal of specific heavy metal cations from waste-water and the use of clinoptilolite, another natural zeolite, for the removal of the soluble ammonium content. Research is active in the field of radioactive waste stream clean-up while have used impregnated alumina to remove a selection of anions from industrial waste-waters[1].

Ion exchange can either remove all ions from a solution or separate different substances. Therefore, complete deionization and selective removal of ionic contamination can be distinguished. The choice depends mainly on the composition of the solution and on the extent of decontamination required. Spent galvanic baths and waste solutions from various production processes generally contain large quantities of various ions which are hazardous to the environment. Frequently only one kind of ion must be removed from industrial waste-waters due either to its toxicity or its substantial value. Selectivity may be achieved by new types of ion exchangers with specific affinity for definite metal ions or groups of metals. It should be emphasized that in most cases ion exchange requires the replacement of the undesirable ion by another one which is neutral in an environment context.[2] The major disadvantage of ion exchange is the need to regenerate the resin after use for recycle. This requires using a concentrated solution, often sodium chloride, to displace the heavy metals from the resin replacing them by either sodium or chloride ions as appropriate. This regeneration process produces a spent regeneration solution containing relatively high concentrations of heavy metals in brine that results in a costly disposal problem. Recent research has been investigating ways of reducing this regeneration problem.

Further development of conventional ion exchangers like cation exchangers based on polystyrenesulfonates and strongly basic anion exchangers have been aimed at high exchange capacity and better chemical, thermal, and mechanical stability. The kinetic capability of ion exchangers has been improved by the macroporous ion exchangers developed in the 1970s. The range of applications of ion exchange has been remarkably extended by the preparation and application of new organic and inorganic ion exchangers.

II.IV.1.1. Cyanide removal by ion exchange

In addition to the methods normally used for the destruction of cyanide in waste-waters there exists another group of techniques in which cyanide is regenerated. There are two categories within these methods of regeneration: chemical methods and processes using ion exchange resins.[3-5] Ion exchange is a versatile operation that has the potential to process cyanide effluents from the gold extraction process, as shown from the basic characteristics and proposals presented by several authors. These studies have led to the development of industrial processes such as Vitrokele[6] and Augment.[7] However, the ion exchange processes are limited by the difficult elution step and this operation needs to be improved to develop an easier, cheaper industrial process.

II.IV.2. ADSORPTION

Many substances can be used as adsorbent for various metal ions. These include activated carbon, alumina, and silica gel. Of these perhaps activated carbon is the most promising.[8] Most heavy metals, (arsenic, mercury) can be removed by adsorption on carbon. To avoid reduced capacity after regeneration, the carbon should be acid-washed prior to reuse.

Commercial activated carbon is obtained from waste plant materials such as coconut shell, wood, coal, etc., often obtained locally thereby minimising transportation costs. Studies have also shown that plant materials can be used to adsorb metals from aqueous solution and a number of laboratory studies have been carried out on treatment of AMD and other industrial effluents. Further information on biosorption is given below Chapter IV.7.1 and in Section 3.[2]

In addition, very inexpensive and readily available substances such as mineral slimes and fly ashes have also been suggested as adsorbents for aqueous metal ions. It should be borne in mind that the key of their successful application will be a demonstration of ability to selectively adsorb specific metals from complex waste-water matrices, followed by elution or other recovery of a metal rich concentrate.[8]

Activated alumina can reduce fluoride-ion levels to less than 2 mg/L,[9] and arsenate can be polished to less than 10 μg/L.[10]

II.IV.3. SOLVENT (LIQUID-LIQUID) EXTRACTION[8]

This is a well established technology for metal recovery from waste-water recycling where it is principally used for large-scale operations where the concentrations of contaminants are high. Solvents, that generally consist of an organic extractant molecule dispersed in a carrier organic diluent, are becoming increasingly selective, allowing specific molecules to be transferred from the aqueous phase while others are retained. However, the capital outlay for such equipment can be expensive, large volumes of organic extractants are required and performance is often limited by hydrodynamic constraints such as flooding and entrainment. There is also the potential for cross-contamination of the aqueous stream with the organic solution.

The overall process consists of extraction of the metal(s) by contacting the organic (solvent) phase with the aqueous waste stream followed by separation of the 'loaded' organic phase from the aqueous raffinate. This loaded organic phase is then further contacted with a second aqueous phase to back-extract or strip the metal and allow the organic phase to recycle to treat more waste-water. The metal ions in the aqueous stripping solution can be recovered for reuse or sale.

Heavy metals can be present in waste-water as either cations or anions. Cations are usually extracted into an organic diluent by simple or chelating organic acidic extractants. Metal anions can be extracted by ion-pair formation with long chain alkylamines or quaternary ammonium compounds in an organic diluent. When the metals are present as ion pairs in the aqueous phase, then organic compounds, e.g. ketones, organo-phosphates or -phosphine oxides, capable of solvating these complexes can be used.

For waste-water with low concentrations of metal ions, such technology is limited by the need for high aqueous to organic phase ratios and ion exchange will generally be preferred. High phase ratios lead to difficulties with design of equipment, and organic losses through entrainment in the aqueous phase. For mixer-settler units, such entrainment is typically in the range of 100-200 ppm, while in column operation this can be reduced to 10-50 ppm depending on the system. This presents a significant cost to the process and the contamination of the aqueous stream with organic compounds. Such losses can be minimised by careful design of equipment and the introduction of coalescers into the circuit to recover the organic phase. At high phase ratios, in excess of 20:1 the performance of column contractors is reduced because of increased axial dispersion, resulting in larger and more expensive equipment. Other instances where solvent extraction processes can be applied to waste-water treatment include the use of a tertiary amine, tris(2-ethylhexyl)amine (TEHA) or a phosphine oxide mixture (CYANEX 923) for the recovery of mineral acids from hydrometallurgical process waste streams.

II.IV.4. MEMBRANE PROCESSES

(further information on principles, equipment and operations in Section 3).[5]

A membrane is a semi-permeable barrier through which only selected chemical species may diffuse. Ho and Sirkar[11] provide a good overview of membrane processes. Historically, membrane technology has had wide application in water treatment and desalination for the production of potable water through reverse osmosis, (RO).[8] However, membrane technology could be considered a relatively new process in industrial waste-water treatment as the development and the applications in this field have accelerated in recent years. Recent research indicates that waste-water reclamation by RO offers great promise for a sustainable reduction in cost, conserving natural resources, as well as marked improvements of pollutant removal efficiency.[12]

The three membrane processes that have found increased interest for application in pollution control as end-of-pipe treatment and for in-plant recovery systems are ultrafiltration (UF), reverse osmosis (RO) and electrodialysis (ED). Although various processes are available for producing a concentrated solution from a relatively dilute feed, each process tends to dominate a particular type of application due to economic as well as technological considerations.

II.IV.4.1. Reverse Osmosis and Ultrafiltration

There is no sharp distinction between UF and RO. Both processes remove solutes from solution much as a conventional filter separates suspended matter from liquid suspension. Unlike a filter, however, the separated phase does not accumulate on the surface of the medium to any great extent, but rather emerges in form of a much concentrated solution while permeate emerges as a diluted stream. In UF the separation is based primarily on the size of the solute which, depending on the particular membrane porosity, can range from about 2 to 10000 nm. In the RO process, the size of the solute is not the sole basis for the degree of removal. The ability of RO membrane to reject electrolytes increases with an increase of valency. Thus among cations, calcium and magnesium are rejected to a greater extent than Na, while for the anions, sulfate is rejected more than chloride. It thus appears that the basis for rejection is more complicated than that of a simple sieve, but the exact mechanism is still being investigated.

Reverse osmosis is clearly based on the principle of osmosis where diffusion of the solvent, or osmotic flow, will continue until the difference of concentration on both sides of the membrane creates a sufficient pressure to counteract the net solvent flow. This natural tendency for osmosis can be stopped and reversed by applying a hydraulic pressure to the solution side so the solvent can be forced to flow from the solution. In order to obtain reasonable flow rates through the membranes, RO systems are operated at from 2-10 MPa while UF systems require only about 70-700 kPa pressures.

Reverse osmosis and ultrafiltration find applications in the recovery of valuable metals in various metal industry waste-waters. In the case of AMD these methods find application in the removal of sulfate.

II.IV.4.2. Electrodialysis[9]

In contrast to reverse osmosis and ultrafiltration, ED employs the removal of the solute, with a small amount of accompanying water, from solution rather than the removal of solvent. The other major distinction is that only ionic species are removed. The advantages of ED are primarily due to these distinctions. Operating costs tend to be lower since less energy is required to transport the salt, as compared with water, because this component is present to a much smaller extent. The fact that only ionised salt will be removed allows the simultaneous separation of these substances from any neutral or un-ionized organic matter that may be present. Although these features are similar to ion exchange, the advantage is that in ED the process is continuous with no regeneration stage hence no chemical additions are required. In ED, unlike the other membrane process, two different membranes must be used together: an anion-permeable membrane that only permits passage of anions, and a cation-permeable membrane to allow passage of cations.

ED can be used to recover metals from plating waste streams, in the metal industry. Thus a closed-loop recovery process incorporating ED and ion-exchange permits complete recovery of nickel, allowing reuse of the dilute stream for rinsing, and recovering the acid required for the regeneration of the ion exchangers. Copper and chromium have also been recovered from etching processes.
Among the emerging membrane processes, (see below) emulsion liquid membranes (ELM), and supported liquid membranes (SLM), have to be highlighted for metal recovery from waste-water.

II.IV.4.3. Overview of emerging membrane processes[1]

II.IV.4.3.1. Emulsion liquid membranes

The concept of a permeable barrier for use in solvent extraction was first proposed by Li in the 1960s in the form of an emulsion liquid membrane (ELM). Ho and Li provide a good review of this technology. ELM technology has been commercialised for the extraction from waste-water of cyanide and zinc. Pilot scale studies have also been carried out for the removal of heavy metal cations such as zinc, cadmium, chromium, copper, lead, palladium and mercury from waste-water, and the removal of anions, such as chlorides, sulfate, selenium, phosphate and chromate. ELMs provide efficient mass transfer in small and medium size applications, particularly when feed concentrations are fairly low. However, issues of emulsion stability and membrane leakage have limited their commercial potential.

II.IV.4.3.2. Supported liquid membranes

An alternate approach to the problems of emulsion stability has been to immobilise the organic liquid phase within a porous structure. The solvent is placed in the pores of a microporous membrane material prior to service by soaking. SLM technique has received much attention in the literature. However, few industrial applications of SLMs have been successfully implemented. Commodore Separation Technologies installed such technology at the Port of Baltimore in 1998 for the removal of 500-1000 ppm of Cr(VI) from groundwater. The effluent water was to contain less than 0.05 ppm Cr(VI), suitable for direct discharge into Chesapeake Bay. However, it appears that environmental standards could not be attained and the equipment has now been removed.

II.IV.5. FLOTATION

II.IV.5.1. Flotation process in waste-water treatment[13]

Flotation had its beginning in mineral (ore) processing and as such has been used for a long time in solid/solid separation applications using stable froths to selectively separate different minerals from each other. Regarding the application of flotation in waste-water and domestic sewage treatment, civil and chemical engineers have used dissolved air flotation (DAF) for a number of years. The main applications have been in the removal of solids, ions, macromolecules, fibres, and other materials from water.

The main differences between "conventional" flotation of ores and flotation applied to water treatment are described below.

The method of producing the gas bubbles to generate micro, medium, or macro-bubbles. It is now widely accepted that medium size and large bubble diameters (300-1500 µm) are optimal for flotation of minerals (fines and coarse particles). Yet, conventional flotation devices do not generate a sufficient number of bubbles smaller than 600 µm. The main uses of micro-bubbles (<100 µm) is in the application of flotation to solid/liquid or liquid/liquid separation. Thus, the distinguishing feature between conventional mineral flotation and flotation in waste-water treatment is that, where extremely small (or even colloidal) particles have to be floated, micro-bubbles are required.

Because the species being floated are usually aggregated colloids rather than dispersed species, high shear rates must be avoided to avoid destruction of the fragile aggregates. This is important in the clarification of effluents and introduces distinct problems not previously encountered in mineral flotation.

The solids content present in the pulp system, whether diluted or not have a wide range of sizes, unlike the feed in mineral processing. A limiting feature of bubbles is their lifting power or carrying capacity so micro-bubbles do not float dense or large particles, especially at high solids content (4-5%, w/w).

The type of separation: i.e. solid/solid/liquid in mineral processing, and solid/liquid, solid/liquid/liquid, or liquid/liquid in water treatment.

In mineral flotation it is necessary to produce a stable froth at the free surface of the flotation cell but in applications to waste-water treatment a stable foam is not required.

In mineral flotation, the overall process is economically attractive as it provides a mineral concentrate but in environmental applications, usually flotation means an extra cost.

Flotation technology can be incorporated in mining and industrial waste-water treatment schemes in the following ways:

- as a unit process (ancillary or main process) to remove contaminants which are not separated by other means. Depending on performance (water quality), process water can be adequately treated and recycled,
- as a treatment unit for floating solids in thickeners (concentrates or tailings),
- as an auxiliary process for bio-oxidation lagoons or sludge thickening in water reuse,
- as a process for removing various organics, residual chemicals, including petroleum, from water,
- as a solid/liquid separation process in acid mine drainage neutralization with lime,

- as a primary treatment unit ahead of secondary treatment units, such as bio-oxidation lagoons for reducing the cost of aerobic digestion,
- as a unit process for sludge thickening.

Technical and economical potential of this process:

- high selectivity to recover valuables (Au, Pt, Pd, etc.),
- high efficiency to remove contaminants: high over-flow rates, low detention periods (meaning smaller tank sizes, less space requirement, savings in construction costs); thicker scums and sludges than in gravity settling or skimming,
- low operating costs with the use of upcoming flotation devices,
- thicker flotation concentrates (6-12% w/w).

III.5.2. Conventional flotation techniques, devices and processes[13]

Some recognized techniques are summarized below to show their main features.

III.5.2.1. Electro-flotation (EF)

In this process the micro-bubbles are generated by the electrolysis of diluted aqueous, conducting solutions leading to the production of gas bubbles at both electrodes. Applications, to date, on an industrial scale, have been in the area of removing light colloidal systems such as emulsified oil from water, ions, pigments, ink and fibres from water.

In water and waste-water treatment, flotation is the most effective process for the separation of oil and low-density suspended solids. Electro-flotation is effective in treating oily waste-water or oil-water emulsions, spent cooling lubricant, waste-water from coke-production, mining waste-water, ground-water, pit waters, colloidal particles, heavy metal containing effluents, gold and silver recover from cyanide solution, and applications to many other water and waste-waters problems.[14]

III.5.2.2. Dispersed (induced) air flotation (IAF)

Here the bubbles are mechanically formed by a combination of a high-speed mechanical agitator and an air injection system making use of the centrifugal force developed in the system. The gas, introduced at the top, and the liquid become fully intermingled and, after passing through a disperser outside the impeller, form a multitude of bubbles sizing from 700-1500 μm diameter. This method, well known in mineral processing, is also utilized in the petrochemical industry, for oil-water separation.

III.5.2.3. Dissolved air (pressure) flotation (DAF)

Reduction in pressure of water, pre-saturated with air at pressures higher than atmospheric, releases the air in the form of bubbles. The pressure reduction is obtained by forcing the supersaturated water through needle-valves or special orifices, producing clouds of bubbles, (30-100 μm diameter) just down-stream of the constriction.

DAF was recognized as a method of separating particles in the early 20th century and since then has found many applications including:

- clarification of refinery waste-water, waste-water reclamation,
- separation of solids and other in drinking water treatment plants,
- sludge thickening and separation of biological flocs,
- treatment of ultra-fine minerals,
- removal of organic solids, dissolved oils and VOCs (dissolved toxic organic chemicals),
- removal of algae; micro-organisms e.g. giardia and cryptosporidium oocysts,
- treatment of humic waters, etc.

The DAF process is by far the most widely used flotation method for the treatment of industrial effluents. It is believed that applications will rapidly expand in waste-water treatment in the metallurgical and mining fields. DAF development has been very rapid in the last decade and many of its earlier limitations are being resolved.

II.IV.6. ELECTROCHEMICAL METHODS[14]

Using electricity to treat water was first proposed in the UK in 1889. The application of electrolysis in mineral beneficiation was patented by Elmore in 1904. Electro-coagulation (EC) with aluminium and iron electrodes was patented in the US in 1909 and was first applied to drinking water on a large scale in the US in 1946. Because of the relatively large capital investment and the high cost of electricity, electrochemical water or waste-water technologies did not immediately find worldwide application. Extensive research, however, in the US and the former USSR during the following half century has accumulated abundant knowledge of the technology. With the ever increasing standards applied to drinking water and the stringent environmental regulations regarding waste-water discharge, electrochemical technologies have regained their importance worldwide over the past two decades. There are companies supplying facilities for treating: metal recovery; drinking or process waters; electroplating effluents, oil and oil-in-water emulsions; etc. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost, but also are more efficient and more compact. For some situations, electrochemical technologies may be an indispensable step in treating waste-waters containing refractory pollutants. Among the established technologies, electrochemical reactors for metal recovery, ED, and electro-flotation have been discussed. Electro-coagulation, electro-flotation and electro-oxidation can be also considered as established technologies while electro-photooxidation and electro-disinfection are promising emerging technologies.

II.IV.6.1. Electro-coagulation

Electro-coagulation involves the generation of coagulants *in situ* by electrically dissolving either aluminium or iron ions from metal electrodes. The generation of metal ions takes place at the anode with hydrogen gas being released from the cathode. The hydrogen gas bubbles thus produced would also help to float the flocculated particles to the water surface. This process sometimes is called electro-flocculation.

Electro-coagulation is efficient in removing suspended solids as well as oil and greases. It has been proven to be effective in treatment of drinking water supplies for small or medium sized communities, for marine operation, and even for boiler water supply for industrial processes where a large water treatment plant is not economical or necessary. It is very effective in coagulating the colloidal material found in natural waters thus reducing turbidity and colour. It can also be used in the removal or destruction of algae or micro-organisms and removal of iron, silicates, humus, dissolved oxygen, etc. Electro-coagulation was found particularly useful in waste-water treatment; petroleum, tar sand and oil shale process waters, oily waste-waters and oil-water emulsions; clay suspensions; and nitrite from waste-waters. The reduction, coagulation, and separation of copper was also effective.

II.IV.7. BIOLOGICAL ION REMOVAL[9]

Naturally occurring biological materials have been found to be effective in the removal of metal ions from waste-waters. Thus some bacteria recovered from acid mine-waters can precipitate dissolved copper in the form of copper sulphide, in the presence of H_2S generated by reducing elemental sulfur with glucose. The following bacteria have been reported as potentially useful in abating pollution: *leptothrix ochracea, clonothrix putealis, siderococcus sp.* and *toxothrix thricogenes*. These micro-organisms, when added to a slow sand filter, can eliminate iron and manganese from water by oxidizing the metals to precipitateable species that can then be removed by the filter.

II.IV.7.1. Biosorbents

(*for more information see Section 3).*[2]

Biological materials are effective at binding or adsorbing metals, including arsenic, present in various solutions. These biological materials cover a wide range of species from shrubs and grasses to mosses, fungi, algae, and bacteria. Additionally, it has been shown that both chemical reaction and microbial metabolism were originally responsible for the formation of the mineral deposits that are currently being mined.

II.IV.7.2. Biological sulfate reduction

Some anaerobic bacteria reduce sulfate to sulfide as a part of their metabolic cycle, such species are termed sulfate-reducing bacteria (SRB). This process can be used *in-situ* or in treatment plants to remove heavy metals and toxic inorganic species to very low concentration levels with a number of advantages. As an example biological arsenic removal uses anaerobic (SRB) and other direct arsenic reducing bacteria to precipitate arsenic from solution as insoluble arsenic-sulfide complexes in simple reactors that can be removed using conventional solid/liquid separation. This process produces hundreds to thousands times less sludge than conventional arsenic precipitation as ferric arsenate but the achievable sludge reduction levels and the full scale capital and operating costs, are both site and waste-water dependent.

II.IV.8. PASSIVE METHODS[15, 16]

Active chemical treatment of AMD to remove metals and acidity is often an expensive, long-term proposition which render consolidated techniques impracticable. Passive processes have received attention as alternatives to conventional methods for treating AMD, particularly for replacing common collection and treatment practices that would be unaffordable for streams with a low flow and seepages. In recent years, a variety of passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated mine waters.

Passive technologies include:

- wet-land and reed-bed technology,
- anoxic limestone drains (ALD),
- successive alkalinity-producing systems (SAPS),
- limestone ponds,
- open limestone channels (OLC),
- and sulfate reduction and biosorption discussed in chapter IV.7 above.

Of these SAPS, limestone ponds and OLC can be considered promising emerging technologies while wetland and ALD are emerging methods that have already been successfully applied.

II.IV.8.1. Wetland technology

Natural wetlands are characterised by water-saturated soils or sediments, with supporting vegetation adapted to the anaerobic reducing conditions in their rhizosphere. Constructed wetlands systems (CWS) are man-made ecosystems that mimic their natural counterparts. They consist of shallow flooded excavations filled with gravel, soil, and organic matter to support wetland plants. The first major engineered wetland treatment scheme dealing with a mine-water discharge was designed and constructed at Woolley Colliery, UK in 1995.

Treatment depends on dynamic biogeochemical interactions as the contaminated water travels through the constructed wetland. Properly constructed wetlands can reduce the effluent concentrations of dissolved metals to meet regulatory limits and have been effectively utilised in many sites to reduce the cost of conventional chemical treatments. Results of using CWS depend on the metal and although it successfully removed Fe, Mn and Al removal was more variable.

The mechanisms of metal retention within wetland include:

- formation of metal oxides and oxyhydroxides,
- formation of metal sulfides,
- retention as organic complexes,

- ion exchange with other cations,[6] and
- direct uptake by living plants.

Other mechanisms may include physical filtration of suspended metal colloids and adsorption/exchange of metals onto algal mats.

Two types of construction currently predominate: “aerobic” wetlands consisting of vegetation, usually *typha*, planted in shallow relatively impermeable sediments comprised of soil, clay or mine spoil and “anaerobic” wetlands consisting of vegetation planted into deep, permeable sediment.

II.IV.8.2. Aerobic wetlands

Aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of iron, aluminium, and manganese oxyhydroxides. Aerobic wetlands are best used in conjunction with water that contains net alkalinity to neutralise the metal acidity. As metals such as Mn and Fe precipitate at different rates, several staged aerobic wetlands must be constructed in series if removal of both metals is to be attempted. Long-term successful treatment by a staged aerobic wetland has been reported for net alkaline water at the Simco CWS in Ohio.

II.IV.8.3. Anaerobic wetlands

Whereas anaerobic wetlands promote metal oxidation and hydrolysis in the aerobic surface layers, they primarily rely on chemical and microbial reduction reactions to precipitate metals and neutralize acidity. The water infiltrates through a thick permeable organic subsurface sediment that becomes anaerobic due to the high BOD. In this region several additional mechanisms for treating the waste-water are present including: metal exchange and complexation reactions; formation and precipitation of metal sulfides; alkalinity generated by the microbial reduction reactions, and continuous formation of carbonate alkalinity from limestone dissolution under anoxic conditions. Since anaerobic wetlands produce alkalinity, their use can be extended to poor quality AMD, with low pH, high Fe, and high dissolved O_2.

II.IV.8.4. Anoxic limestone drains (ALD)

These consist of buried cells or trenches of limestone into which anoxic water is introduced. The limestone dissolves in the acid water, raises the pH and adds alkalinity. Unlike under oxidising conditions, the limestone does not become coated with iron hydroxides because under anoxic conditions, Fe^{2+} does not precipitate as $Fe(OH)_2$ at pH 6. Once the water containing excess alkalinity reaches aerobic conditions at the ground surface, the metals oxidise and precipitate while the water remains at approximately pH 6. The Tennessee Division of Water Pollution Control and the Tennessee Valley Authority began building ALD in 1989 originally as pre-treatment of water flowing into CWS.

II.IV.9. BAUXSOL TECHNOLOGY[17-19]

The red mud generated as a by-product of the Bayer processing of bauxite consists of hematite, boehmite, quartz, sodalite, and gypsum and is characterised by high alkalinity (about 13). The possibility of utilising this red mud for the remediation of contaminated liquid effluents has been the object of several studies focused at trapping the metals and neutralizing the acidity. The results of such studies have been exploited in several waste-water treatment processes, among which the Bauxsol technology has been commercially exploited by Virotec.

Virotec International Ltd. (Australia) patented a process of treating the red mud with sea-water and pelletisation to produce Bauxsol, a complex mix of Fe and Al oxyhydroxides and alumino-hydroxy-carbonates. The patented technology is based on sea-water treatment which converts "soluble alkalinity" (mainly sodium hydroxide) into low solubility minerals (essentially Ca and Mg hydroxides, carbonates and hydroxycarbonates), thus reducing the red mud pH from >13 to <9). Virotec has commercialised, ViroMine, a series of specific products for the mining industry, including Neutra B™, Acid B™, Acid B Extra™, Alka B™, and Cya B™.

AMD treatment with these products essentially consists of a staged process which allows metal binding reactions to occur in the optimum pH range. In each stage, the appropriate fine-grained Bauxsol reagent is added to the metal contaminated waste-water and after 48 hours the spent Bauxsol sediments. The Bauxsol reagents chemically react with the heavy metal contaminants, through a binding mechanism resulting in metal sequestration within the fine Bauxsol particles as insoluble minerals. The mechanism by which the metals are trapped is probably adsorption due to the high porosity - surface area/volume ratio and the high charge/mass ratio of the Bauxsol particles. At the same time, these particles neutralise any acidity in the water, through slow reactions with the low solubility carbonate, hydroxide, and hydroxycarbonate minerals.

Laboratory studies and on-site applications have demonstrated that Bauxsol Technology is effective in treating acid and trace metal release from sulfidic mine tailings, sulfidic waste rock, and acid sulfate soils and could be used to prevent AMD following closure of mines.

An important advantage that this technology offers in comparison to the conventional precipitation processes is that the chemical stability of the residues is increased due to the chemical and physical adsorption of the metals on the surface of iron oxides which constitute more than 30 % of Bauxol. Moreover, as proved in recent studies, the sediments produced can be re-vegetated. In the light of the practical applications of Bauxsol Technology on "tailing ponds", simultaneous water purification - soil remediation - environmental restoration can be obtained, more effectively and at lower cost than other technologies.

Further studies on pilot plant scale should be carried out to verify the possibility of utilising Bauxol in continuous-flow reactor which is the typical technology used in Europe where an AMD dam is not feasible. A multiple stage continuous process could be the best application for the Virotec series of products.

However, in considering the utilisation of Bauxol technology in continuous operations, the following points should be considered:

- Bauxsol has a neutralisation capacity 4 times less than lime and 5 times less than soda and the average requirements of Bauxol is about 5 kg/m^3 of water, depending on metal concentration and pH of the AMD,
- although the TCLP test shows that the spent Bauxsol is not toxic, disposal of the spent Bauxsol must be in accordance with national regulations. Thus 16 day leaching tests, equivalent to the column test, have shown that spent Bauxol cannot be re-used but must be landfilled as industrial waste.

References to Chapter II.IV

1. S E Kentish and G W Stevens, *Innovation in separation technology for the recycling and re-use of liquid waste streams,* Chem. Eng. J., **84**, 149-159, (2001)
2. A Dabrowski, Z Hubicki, P Podkoscielny and E Robens, *Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method*, Chemosphere, **56**, 91-106, (2004)
3. M M Botz and S Gason de Parodi, *Removal of copper from cyanide leach solutions*, in Randol Copper Hydrometallurgy Roundtable, (1997)
4. M M Botz and J A Stevenson, *Economics of cyanide recovery and destruction processes*, Unified Engineering, (1994)
5. C C Frey, W R Hatch and M K Witte, *Recovery of cyanide from waste-waters by an anion exchange process*, US Patent 4732609 (1988)
6. C A Fleming, *The potential role of anion exchange resins in the gold industry,* in EPD Congress of the Minerals, Metals and Material Society (1988)
7. M R Paterson and A E Jenkins, *Vitrokele resin technology for the recovery of complexed and free cyanide*, Signet Engineering, (1996)
8. R W Smith, *Liquid and Solid Wastes from Mineral Processing Plants*, Mineral Processing and Extractive Metallurgy Review **16**, 1-22, (1996)
9. V Cavaseno, *Industrial Wastewater and Solid Waste Engineering*, Chem. Eng. Mag., Mc Graw-Hill Publication Co. (1980)
10. http://www.rwateterguy.com
11. W S W Ho and K K Sirkar, Membrane Handbook, Van Nostrand Reinhold, New York (1992)
12. H A Qdais and H Moussa, *Removal of heavy metals from wastewater by membrane process : a comparative study*, Desalination, **164**, 105-110, (2004)
13. J Rubio, M L Souza and R W Smith, *Overview of flotation as a wastewater treatment technique*, Min. Eng., **15**, 139-155 (2002)
14. Guohua Chen, *Electrochemical technologies in wastewater treatment*, Sepn. Purif. Technol., **38**, 11-41, (2004)
15. Metcalf and Eddy, Wastewater Engineering: Treatment, Disposal, Reuse, Mc Graw-Hill International Edition (1991)
16. J G Skousen, A Sexstone and P F Ziemkiewicz, *Acid Mine Drainage Control and Treatment,* in Reclamation of Drastically Disturbed Land, Agronomy Monograph no. 41, ASA, CSSA, and SSSA, Madison, WI, p. 131-168, (2000)

References to Chapter II.IV

17. C Brunori, C Cremisini, P Massanisso, V Pinto and L Torricelli, *Reuse of a treated red mud bauxite waste: studies on environmental compatibilità*, J. Hazard. Mat. **B117**, 55-63, (2005)
18. H S Althundogan, S Althundogan, F Tumen and M Bildik, *Arsenic adsorption from aqueous solutions by activated red mud*, Waste Man. **22**, 357-363, (2002)
19. http://www.virotec.com

II.

CHAPTER II.V: PROMISING NEW TECHNIQUES

The following technologies have been studied at laboratory and pilot plant scale:

- Membrane technologies: nanofiltration.
- Flotation: nozzle flotation, column flotation, centrifugal flotation, jet flotation.
- Passive methods: successive alkalinity-producing systems (SAPS), limestone ponds, open limestone channels (OLC).
- Electrochemical methods: electro-photooxidation and electro-disinfection also are considered to be promising technologies.

II.V.1. MEMBRANE TECHNOLOGIES

II.V.1.1. Nanofiltration[1]

Nanofiltration is a promising technology that combines pressure filtration with the use of a negatively charged membrane. The more negatively charged multivalent anions and higher molecular weight organic compounds are retained, while monovalent salts pass through the membrane. Some applications include partial softening of feed water, removal of contaminants from water or acid streams, and pre-treatment for reverse osmosis or other high purity systems. With both reverse osmosis and nanofiltration, the membrane operates primarily through size exclusion and so selectivity for specific metal ions is limited. Much greater selectivity in waste-water treatment can be obtained by combining the physically selective permeability of membranes with the chemically selective separation provided by solvent extraction. In this example, a membrane is placed between a waste stream and a suitable solvent, and mass transfer of selected chemical species occurs across this barrier.

II.V.2. FLOTATION[2]

II.V.2.1. Nozzle flotation (NF)

This process uses a gas aspiration nozzle (either an eductor or exhauster) to draw air into recycled water, which in turn is discharged into a flotation vessel (similar to conventional dispersed-air equipment), to develop a two-phase mixture of air and water with bubbles 400-800 μm in diameter. Advantages claimed for the nozzle units, over induced air flotation (IAF) systems, are the following:

- lower initial costs and energy use as a single pump provides both mixing and air supply,
- lower maintenance and longer equipment life because the unit has no high-speed moving parts.

Reported applications have been exclusively in the petrochemical industry for the separation of oil/water emulsions and treatment of oily metal-laden waste-water.

II.V.2.2. Column flotation

This is still a subject of great interest in mineral processing with a steadily growing number of research studies and industrial applications. The design of the column depends on the application. Thus in the mineral processing area the feed slurry enters the column about one-third from the top and descends against a rising swarm of bubbles generated by a sparger, whereas in waste-water treatment, the feed enters at the top of the column in the middle of the “concentrate” product.

New developments in column technology include: external gas spargers operating with and without the addition of surfactant or frothers; columns with internal baffles and coalescers for oil recovery. In the presence of the surface-active reagents, micro-bubbles can be obtained as in the Microcel column. Applications of column flotation have been reported in the field of oil removal in production waters, and in the recovery of heavy metals precipitates.

II.V.2.3. Centrifugal flotation (CF)

In this system the separator and contactor can be either a hydrocyclone or a simple cylinder in which a centrifugal field is developed. Aeration occurs by either injecting air or by suction, through flow constrictions, such as static mixers or nozzles, wehereby medium size bubbles with 100-1000 μm diameter are generated.

The air-sparged hydrocyclone (ASH) can be classified as a centrifugal flotation unit. It consists of an aeration system where air is sparged through a jacketed porous tube wall where it is sheared into numerous small bubbles by the high-velocity swirl flow of the aqueous phase. Environmental applications of ASH flotation have been recently reported. An advanced ASH type of flotation has been reported in applications to remove oil, grease, BOD, etc.

Bubble accelerated flotation (BAF) uses the contactor-separation concept with very low retention times in the contactor. Depending on the bubble generation system the authors report devices named: induced air BAF, vacuum BAF, and electro-flotation BAF.

II.V.2.4. Jet flotation

This cell appears to have a great potential for solid/liquid separations and for liquid/liquid separations as well as in mineral processing. Its main advantage is its high throughput, high efficiency and moderate equipment cost. Moreover, with no moving parts, the jet cell has low power consumption and low maintenance costs. The cell consists of an aeration/contact zone (the down-comer), a bubble-particle or aggregate disengagement zone and a cleaning or froth forming zone.

The medium size bubbles formed in this cell may be 100-600 μm in diameter. Problems with process accuracy have been recently solved and its use has been extended to waste-water treatment, recovery of solvent extraction liquors and municipal water treatment.

II.V.2.5. Cavitation air flotation (CAF)

Cavitation air flotation utilizes an aerator (rotating disc), which draws ambient air down a shaft and injects "micro-bubbles" directly into the waste-water. CAF can be utilized in the food industry, especially the milk industry, painting installations, and tanneries to remove suspended solids, fats, oils, greases, BOD and COD. However, there no fundamental work has been reported with this flotation technique.

II.V.3. PASSIVE METHODS[3,4]

II.V.3.1. Successive alkalinity-producing systems (SAPS)

Successive alkalinity-producing systems (SAPS) consists in treating acid water, 1-3 m deep, in a pond lined with limestone (0.5-1m) over which is a layer of organic compost (0.2-0.3 m). Below the limestone a series of drainage pipes conveys the water to an aerobic pond where metals are precipitated.

II.V.3.2. Limestone ponds

Limestone ponds can be constructed over an up-welling flow, or seep of AMD or an underground mine discharge. Limestone is placed in the bottom of a pond through which the water flows upward. The pond should be sized and designed to retain the water for 12-24 hours for limestone dissolution and to retain the seep and limestone under water.

II.V.3.3. Open limestone channels (OLC)

Open limestone channels (OLC) are another means of introducing alkalinity into acid water. Past assumptions have held that armoured limestone, i.e. limestone covered with iron or aluminium hydroxides, ceases to dissolve. Thus found that armoured limestone was 50-90% effective in neutralising acid compared to un-armoured material. OLC show promise for neutralising AMD in watershed restoration projects where one-time installation costs are incurred, little to no maintenance cost is required, and systems do not have to meet specific water quality standard.

References to Chapter II.V

1. S E Kentish and G W Stevens, *Innovation in separation technology for the recycling and re-use of liquid waste streams,* Chem. Eng. J., **84**, 149-159, (2001)
2. J Rubio, M L Souza and R W Smith, *Overview of flotation as a wastewater treatment technique*, Min. Eng., **15**, 139-155. (2002)
3. Metcalf and Eddy, Wastewater Engineering: Treatment, Disposal, Reuse, Mc Graw-Hill International Edition (1991)
4. J G Skousen, A Sexstone and P F Ziemkiewicz, *Acid Mine Drainage Control and Treatment,* in Reclamation of Drastically Disturbed Land, Agronomy Monograph no. 41, ASA, CSSA, and SSSA, Madison, WI, p. 131-168, (2000)

III.

INDUSTRIAL LIQUID EFFLUENTS IN THE TEXTILE INDUSTRY

Cluster Leader

Institut Francais du Textile et de I'Habillement (IFTH), ECULLY, France - R. Martinetti.

Members

Centro de Investigaciones Energéticas, Medioambientales y Tecnologicas (CIEMAT), Madrid, Spain - J. Malato, S. Blanco.

Deutsches Zentrum für Luft und Raumfarht e.V. (DLR), Köln, Germany - C. Sattler.

Tecnotessile Societa Nazionale di Ricerca Tecnologica r.l, Prato, Italy - I. Ciabatti, F. Tognotti.

University of Applied Sciences Cologne, Gummersbach, Germany - M. Bongards, A. Ebel.

University of Applied Science Gelsenkirchen, Germany - W. Schmidt.

Zenit GmbH, Muelheim an der Ruhr Zenit, Germany - P. Wolmeyer, U. Birk.

INDEX

III.1. INTRODUCTION

III.1.1. General presentation

Textile industry is one of the longest and most complicated industrial chains (from the fibre to the end-product) in manufacturing industry (see Figure 1.1).

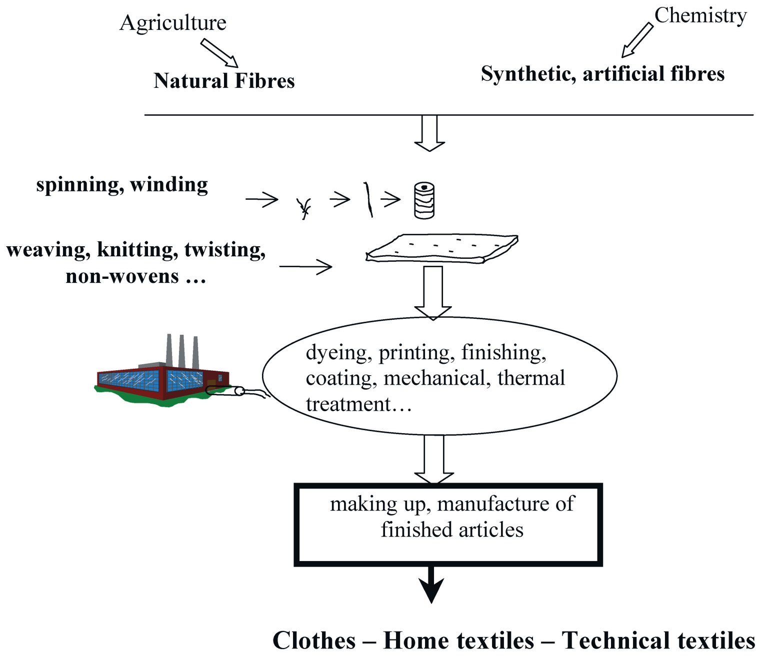


Figure 1.1. Outline description of the textile production chain

The textile and clothing chain involves a large number of sub-sectors that cover the entire production cycle from the production of raw materials (fibres, filaments) to semi-processed materials (yarn, woven, and knitted fabrics) to final products.

This sector is fragmented and heterogeneous and is mainly represented by SME-SMI. The uses of textiles are very large with the three main markets: clothing, home textiles, and technical textiles. Most of textile SMEs are not integrated that means they not cover the whole production cycle.

In 2000, The EU textile and clothing industry achieved a turn over of 198 billion euros, involving 11400 companies employing 2.2 million people (Source: Euratex 2002). Textile processing is globally one of the most important sectors for both production and employment.

In Europe, Italy is the leading producer followed by Germany, UK, France, and Spain and these countries cover 80% of European textile production. The textile industry involves a wide number of sub-sectors, covering the entire production cycle: production of raw materials (man-made, natural, and synthetic fibres); semi-processed (yarn, woven, knitted fabrics, non-woven materials, finishing processes); final products (clothing, textiles for the home and industrial use).

Currently, the European textile industry is going through a major crisis due to competition from Asia caused by very low labour costs in that region. Today we could consider than more or less 50 % of textile production is done in China.

III.1.2. Textile finishing sector

This step is the main pollutant because of the large amount of water and chemicals used to prepare, wash, dye (photos 1.1 and 1.2), and finish textile fibres or fabrics. The main processes in the finishing sector involve: bleaching, dyeing, printing, finishing (chemical or physical treatments), and coating.

The main aim of textile finishing is to confer to fabrics the visual, hygienic, comfort, aesthetic features that the consumer and the market demand. It is also influenced by fashion and seasons (colours, fibre composition, thickness, etc.).

Photo 1.1. Dyeing machine overflow

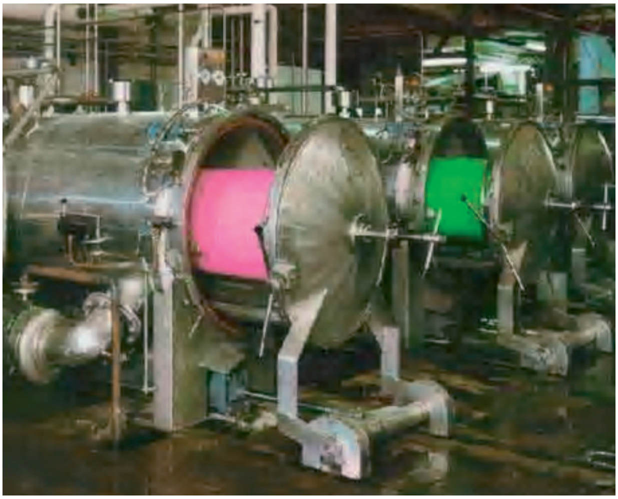


Photo 1.2. Dyeing machine - Kier

III.1.3. Background and current EU legislation for industrial liquid effluents

III.1.3.1. Water directive

This directive was passed on the 23th October 2000 and published on the 22th December 2000. This is a major text into which EC members agree to a process of objective water quality with the aim of requiring that the aquatic environment must be in a good state by 2015 at the latest. The quality of the water will be appraised according to regulations and current water uses, at the basin level.

This means that if a hydrographical basin is considered as more sensitive or vulnerable, restrictions and constraints will have to be higher. This directive sets the objective of reaching a good ecological state, so the use of biodegradable, natural, harmless substances are recommended in order to attain a high level of water quality.

III.1.3.2. IPPC directive

In summary the authorization is periodically reassessed and must contain emission limits for polluting substances (especially those indicated in Annexe II) and prescriptions as regards water preservation. Such limits are normally based on the Best Available Techniques. They also take in account the characteristics of the installation as well as its geographical location and the sensitivity of the local environment.

Thus, in view of the local situation, such as decentralisation of the authorities, vulnerability of environment, water quality objectives, important differences could occur from country to country and from one region to another in the EU (e.g. Italy, Germany). Table 1.1 lists some current limits of importance to the textile industry.

Basically, with the new water and IPPC directives it could reasonably be assumed that the regulations should be harmonised among the 25 EC members and will tend to median values.

Products and substances considered as dangerous for the aquatic environment.

Article 16 of the new water directive (2000/60/CE) enforces reduction (with elimination in under 20 years) of priority toxic substances from the aquatic environment. This new directive 2000/60/CE abrogates directive 76/464/CE (list I and list II). On 7th June 2001, the European Parliament adopted a list of 33 priority toxic substances for the aquatic environment.

III.1.3.3. Comparison of Emission Limits[3] for some countries

mg/L	Belgium	France	Germany	Italy	Netherlands	Spain	U.K.	Denmark	Finland	Estonia	Slovenia	Poland	Australia	Japan
$\mathrm{COD}^{\dagger}$	400	125-300	160	160		125		75	30-50% removal	160	110	125		120
COD^{*}	800-5000	2000		500	200-400	1000	1500							
$\mathrm{BOD}_5^{\dagger}$	30	30-100	25	40		25	15-25	15	90-95% removal	15-25	35	25	20	120
BOD_5^{*}		800		250		300								
$\mathrm{SS}^{\dagger}$	50-100	35-100		80	20	35	20-60		35	35	35	35	30	25-100
SS^{*}		600	200-2180	200	20-100	500	450							
$\mathrm{N}^{\dagger}$ (NH_3)		15-30	20	20		15		8 (total N)		15 (total N)	10 (total N)	10 (total N)		60 (total N)
N^{*} (NH_3)		50	2	30		20			10 (total N)					
$\mathrm{P}^{\dagger}$ (total)		2-10		10		2		1.5	2	2	2	2		80
P^{*} (total)		50		10		15								

Notes: † limits for discharge to rivers or human water resources;
* limits for discharge to sewers or public waste-water treatment works.

<u>Comments on table 1.1.</u> Note some differences between countries and local situations. Pollution limits differ from country to country but also within the same country. The emission limits mainly depend on: the parameters of pollution, the kind of emission (urban or industrial effluent); the industrial sector (e.g. pulp and paper); the local situation (local policies, local sensitivity of environment); the location for discharge (land, water human resources, sewage works, seas, etc.).

To be complete, it would be certainly useful to refer to the whole reference and the official text (directive, law, decree). Noting that even the textile sector has not often its own legislation (different from paper, plating, etc), the limit values are not so different from one country to another.

III.2. TREATMENT PROBLEMS

III.2.1. Generalities

The environmental impact of textile waste-water is mainly the result of its high chemical oxygen demand (COD) as well as high intensity of colour. Waste-water is the major environmental problem for the textile finishing, dyeing, and printing industries together with other issues such as solid wastes (textiles, packaging, chemicals) and emissions of volatile organic compounds (VOC).

Pre-treatments (washing, bleaching, desizing), dyeing and finishing of fibres, usually require large amounts of water and a large variety of chemicals. Variations in the fabric quality, treatment process, kind of machine, influence of fashion and season, result in large fluctuations in daily flow rates and pollutant concentrations.

Generally, the majority of the textile mills discharge their effluents into municipal or industrial (individual or collective) waste-water plants. In Europe environmental law is becoming stricter and requires efficient pre-treatment and/or tertiary treatment in addition to the normal effluent treatment processes before being discharged. Due to new severe regulations, textile SMEs face problems in selecting the appropriate treatment technologies that are also economically acceptable.

III.2.2. Characteristics of textile liquid effluents

The main characteristics of textile effluents can be described as follows:

- high water consumption: 80-100 m^3/t of finished textile (average values),
- large range of organic chemicals, soluble or insoluble (salts, acids, alkalis, dyes, pigments, oxidizing and reducing agents, detergents, hydrocarbons, urea, ammonia, AOX, etc.),
- high COD levels: 115-175 kg COD/t of finished textile,
- poor biodegradability: COD/BOD_5 = 3-6,
- heterogeneous and variable in quality and toxicity,
- but generally suitable to be combined with a municipal waste-water activated sludge plant.

It is important to emphasise that the heterogeneity of textile effluents depends on the type of fibre (cotton, wool, synthetic artificial, blends, etc) being treated. Indeed, effluent quality depends further on the composition of the fibre, machines, processes (short bath, continuous, or discontinuous treatment), and chemicals used, so that the associated pollution will vary from one mill to another. This variability is also accentuated and influenced by fashion and the season.

The majority of dyeing or printing mills are not the manufacturers of the textiles being treated. Thus, an important part of the pollution load (30-50% of the COD) results from fabric pre-treatment operations such as desizing and bleaching. Because globalisation influences the purchasing of raw textiles, the natural chemicals or oils applied during spinning are very different depending on the country of origin.

For textile mills a convenient waste-water system should reach high performance levels for the removal of: COD, BOD_5, SS (suspended solids), N, P, hydrocarbons, detergents, and colour, achieving the appropriate effluent discharge regulation levels, and able to treat economically high volumes of effluents (500-20,000 m^3/day) with reasonable associated costs (e.g. investment, operating costs, maintenance, etc.).

At the laboratory scale, it is often easy to check and treat numerous parameters to reach high treatment efficiency. However on an industrial scale it is more difficult, mainly because of the variability of the released chemicals. On the other hand it should be realised that the function of the textile trade is to produce textiles not to treat water. So, the selected waste-water technology should be as simple and as autonomous as possible.

So the waste-water treatment strategy has to take into account two complementary objectives:

- conformity with the legal discharge regulations,
- provision of high quality water for recycling, aiming to zero liquid waste on site.

Factors that can have a positive effect on the downstream treatment operations include: upstream and preventive actions in optimizing the process; selection of treatment options (BAT, clean technologies); segregation treatment of specific baths; etc. Therefore as often as possible a management strategy based on the BAT concept should be encouraged involving:

- chemical management (ecological criteria), biodegradability of substances used (sizing agents, tensides, dyes, etc.),
- process optimisation (decreased water consumption, limiting or preventing resulting pollution),
- selection of textile support (absence of pesticides in cotton fibres and wool).

III.3. OPTIMUM AND HIGHLY EFFICIENT WASTE-WATER TREATMENT TECHNIQUES IN THE TEXTILE INDUSTRY

III.3.1. Introduction

The environmental concern over the discharge of textile waste-water is mainly related to its high chemical oxygen demand (COD) and high intensity of colour. In Europe, due to increasingly severe regulations, textile SMEs are facing problems in selecting an appropriate treatment technology that is also economically acceptable.

Nowadays, as noted above waste-water treatment strategies have to take account of two complementary objectives:

- conformity to discharge regulations,
- provision of a high ratio of water recycle and a tendency to zero liquid waste on site.

Different techniques involving physical, chemical, and biological processes are presented below. Due to the diversity of the composition of textile effluents and of the local discharge regulations, purification objectives are often quite different from one mill or country to another. Therefore several kinds of treatment could be appropriate. A lot of publications are related to laboratory studies and to the combination of techniques to reach major objectives such as COD removal, total decolouration, and water recycling.

The different purification technologies[2,3,7,8,9,10,12,13,14] for the textile sector that are readily available and efficient include: physico-chemical treatment, biological treatment (activated sludge), membrane filtration techniques (UF, NF, RO), oxidising and degradation techniques (ozone, UV, photocatalysis), adsorbents (activated carbon, wood powder).

III.3.2. Physico-chemical treatment

III.3.2.1. General principles

Coagulation-flocculation is a treatment, which by addition of a chemical destabilizes small particles in suspension (coagulation). Such particles after destabilization (electrical neutralisation), tend to gather and form coagulated “flocs” 20-50µm in size, which can be separated by decantation or filtration. Flocculation reagents, consisting of long chain polymers or polyelectrolytes, reinforce the floc formation and cohesion.

Basically the current reagents are:

- metallic salts (Fe, Al) for coagulation,
- organic polymers (e.g. polyacrylamides, polyamines, copolymers, etc.) which ensure cohesion of the agglomerates during flocculation.

Flocculation agents are specially selected to maximise the removal of COD and colour, and to minimise sludge formation. In most cases, the best performances are obtained with a combination of aluminium sulfate and iron chloride salts.

The final choice depends on laboratory scale treatability tests on the effluent. Sulfate is considered as less of a problem than chloride because of corrosive problem with chlorides and possible AOX formation during sludge incineration.

A variant of physical-chemical purification consisting of the oxidation of soluble Fe, Al electrodes, (electro-coagulation, electro-flotation) has been used for many years. In addition to the production of Fe and Al ions, oxidising and reducing effects at the electrode surfaces with the emission of H_2 and O_2 have a positive effect on decolouration. Current removal processes are described in Table 3.1.

Before being accepted in waste-water treatment units, the effluent should be subjected to a pre-treatment step (Figure 3.1) that enables the delivery of an effluent with stabilised and homogenous parameters such as temperature and pH. The physical-chemical purification system relies on several operations: coagulation, adsorption, flocculation, and separation.

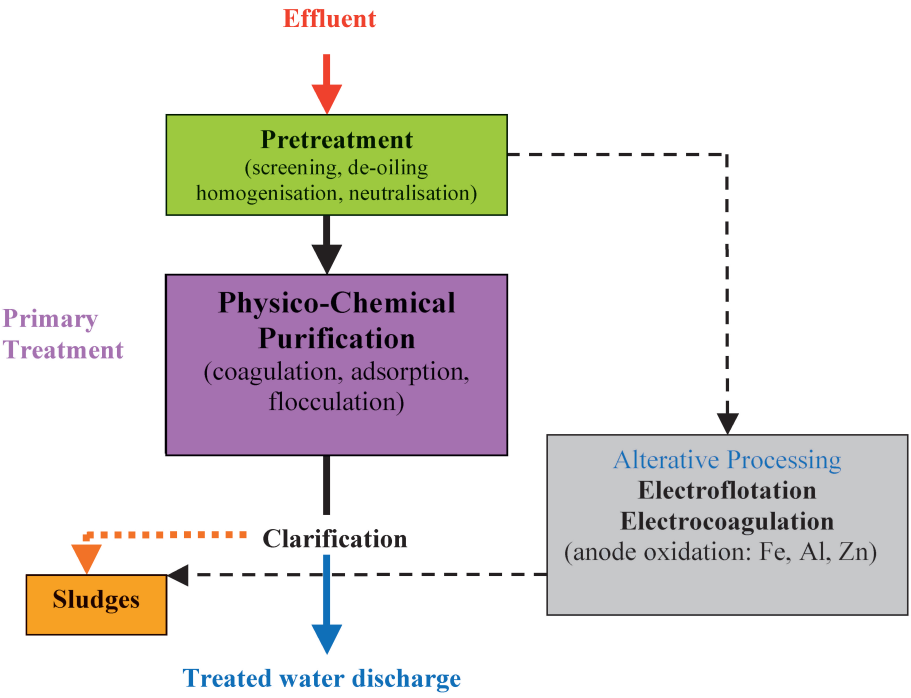


Figure 3.1. Physical-chemical waste-water flow diagram

III.3.2.2. General performance

Physical-chemical purification is only a partially effective treatment and would not permit common discharge regulations to be reached (Table 3.1). In general this system produces a large quantity of sludges that are expensive to eliminate and difficult to dehydrate.

Electro-coagulation or electro-flotation[9] could provide a good alternative to traditional processes. For example due to the high efficiency in colour removal it could be applied to effluents with low flow rate, from printing processes. But the electrical power consumption is quite high 3-6 kW/m^3. In all cases physical-chemical treatment has to be combined with another purification step such as activated sludge, activated carbon, ozone, membrane filtration to improve purification.

	Traditional coagulation flotation system	Electro-coagulation system
COD	35-60 %	40-70 %
BOD_5	20-40 %	20-40 %
Colour	< 20 % (more if insoluble dyes)	50-90 % (more if insoluble dyes and higher energy)
Comments		High electrical consumption (3-6 kW/m^3), little industrial application

Table 3.1. Current performance of physical-chemical treatments

Of particular concern for the textile sector is the treatment of insoluble chemicals and concentrated effluents and for such applications physical-chemical processing only gives partial purification and requires further treatment processing before discharge limits are reached. Also large amounts of sludge that are difficult to treat or eliminate are produced.

III.3.2.3. Textile sectors concerned

Finishing mills (dyeing and printing).

III.3.2.4. Level of industrialisation

Even though biological treatments are mainly used to treat textile effluents, physical-chemical techniques may also be used. Most often it is used in combination with activated sludge processes.

III.3.2.5. Economic data

***Note**: it is very difficult to give real and representative data because of the diversity of textile mills and local conditions (e.g. new or old installations, topography, energy price, etc), so the following figures must be considered as indicative.*

For treating 1000 m^3/day of effluent:

Chemical-physical unit: capital cost 700-900 k€; operating costs*: 0.3-0.5 €/m^3

The following estimation costs could be proposed for treating 1000 m^3/day:

- physical-chemical treatment alone:
  capital cost: 700 K€-1 M€; operating costs: 0.3-1 €/m^3

- physical-chemical treatment in combination with biological treatment†:
  capital cost: 1.1 M€-1.8 M€; operating costs: 0.5-2 €/m^3

(*) operating costs = energy, chemicals, sludge elimination, labour costs.

(†) as noted this technique could be used in combination with other waste-water treatment such as biological or membrane processes.

III.3.2.6. Comments / BREF textile document and BAT

Physical chemical treatment is mentioned as BAT in the BREF document for textiles, especially for printing effluents. Combination with biological treatment is also mentioned as BAT to reach high effluent purification.

III.3.3. Biological treatment

III.3.3.1. General principles

Treatment of waste-waters by aerobic biological processes allows the removal of suspended and dissolved organic substances.

This treatment is suitable for biodegradable effluents through biochemical degradation with micro-organisms. Such treatment exploits bio-absorbance and metabolic transformation processes of colonies of micro-organisms that develop in a controlled way under aerobic conditions. These micro-organisms could either be fixed on specific supports (beds) or in suspension in a tank (activated sludge). In both cases the effluent is contacted with the microbial mass and oxygen in an aeration tank. Turbulence in the tank is maintained by special aerators to keep the microbes in suspension and highly aerate and oxygenate the sludge in order to provide biological oxidation.

As a result of these processes, the suspended and dissolved organic substances are partly mineralised and partly transformed into solids forming a sediment that can be removed by gravity; therefore, treatment consists of two phases: first aeration and then settling.

To maintain a constant quantity of active micro-organisms, sludges are recycled from the clarification tank to the aeration tank with surplus sludge removed and disposed of by partial dehydration and incineration, or to landfill.

This process is designed to treat organic matter and could be applied to nitrogen or phosphorous containing materials by alternating aeration and anoxic phases.

a) Biological activated sludge

In the biological activated sludge process (Figure 3.2), aeration is achieved by a process involving continuous mixing of a suspended biomass, in which the bacterial mass is dispersed in the liquid to be treated; the bacterial mass and the waste-water together constitute the so-called mixed liquor. The biological activated sludge process may be applied whenever a bio-oxidative process is required (photos 3.1 and 3.2). The process is classified in various ways according to the particular phase of the metabolic mechanisms that occur and/or the flux scheme e.g. differentiated aeration plant; complete mixing plant; contact and stabilisation plant.

During the bio-oxidative process the non-sedimenting suspended solids and the dissolved solids are transformed into a sludge that is extracted to be sent either to the sludge treatment plant from the bottom of the settling tank or, according to other schemes, directly from the aeration tank.

A part of the sludge is recirculated to the aeration tank to provide appropriate time for the mixed liquor in the aeration tank (the so-called "sludge age") to complete the bio-oxidative processes. Furthermore, extracted sludge recirculation allows the volume of the aeration tank to be reduced, since the hydraulic retention time in the latter is much lower than the age of the activated sludge inside the tank.

The biological activated sludge process removes the majority of the Biological Oxygen Demand (BOD) and suspended solids found in waste-waters.

Photo 3.1. Textile waste-water plant (activated sludge)

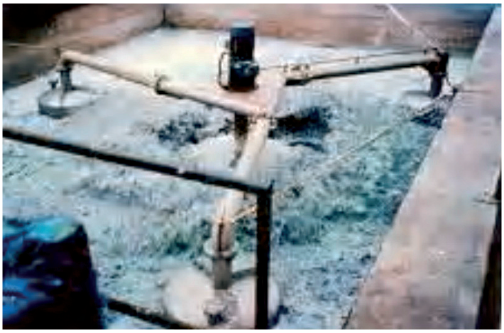


Photo 3.2. Activated sludge

b) Other biological systems

Bacterial beds and anaerobic treatments are considered less effective on conventional textile effluents but they could be appropriate for specific effluents.

Lagoons represent another example of biological treatment. In this process the concentration of micro-organisms is less important than in activated sludge.

Although the activated sludge system gives good results and offers higher guarantees superior to those obtained by physical-chemical processing (Table 3.2), biological treatment alone is insufficient to provide reusable water for industrial recycle.

Therefore additional tertiary treatment steps have to be added to waste-water treatment plants to produce an effluent of higher quality. Such tertiary treatment processes include for example: ozonization, membrane treatment, etc.

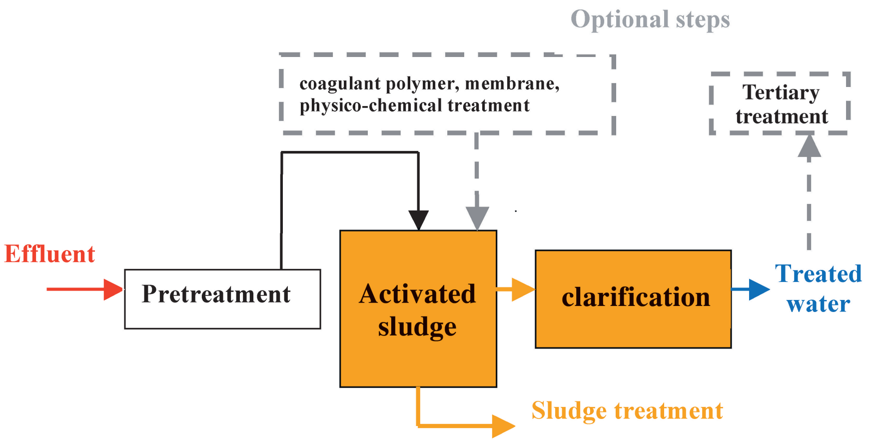


Figure 3.2. biological activated sludge
(examples of common additional treatment steps are given in outline)

c) Secondary and tertiary treatment processes

As noted above, to produce high quality water, the addition of secondary and/or tertiary treatment will be necessary. The most current schemes consist of mixing *biological and physical-chemical technologies*. This association of techniques increases the overall efficiency having a positive influence on both COD and colour removal.

Recent developments carried out by IFTH, have demonstrated on an industrial site, that improvements of activated sludge performance, especially for decolouration, are possible without high added investment by adding a *specific polymer*.[8]

The novelty of the process is to introduce the polymer into the activated sludge. Optimal decolouration is usually reached with a polymer concentration of 30 ppm. This concept is promising at several levels: it is cheap, does not increase the sludge volume, and has a positive effect on strong removal of residual COD. A French engineering company (ETSO) based in Mazamet, has implemented and commercialized this product on an industrial scale.

Membrane bioreactor system (Figure 3.3) represents another example of the interest in combining two different techniques. With this system, the activated sludge is filtered on the membrane module and continuously recycled giving improved performances over the traditional activated sludge process for removal of COD, colour and SM.

The membrane bioreactor also:

- reduces aerator size;
- removes the clarification step while reducing the sludge production;
- facilitates polishing treatment, due to the absence of suspended solids.

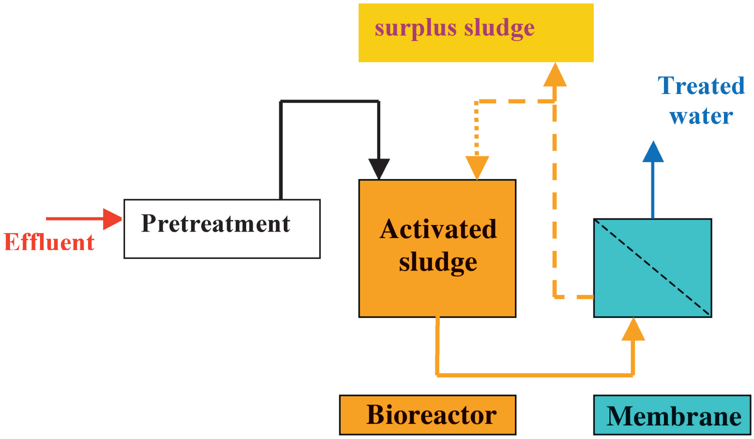


Figure 3.3. Membrane bioreactor

As the retention time is increased, it has a positive effect on weakly biodegradable compounds. But, due to the cost of membranes and the limited flow rates (60-100 L/h/m²) the membrane bioreactor is considered more appropriated for waste-water volumes less than 500 m^3/day.

Efficiencies for different biological purification systems are shown in Table 3.2.

III.3.3.2. General performance

	Activated sludge	Physical-chemical + Activated sludge	Activated sludge + Physical-chemical	Membrane bioreactor
COD	60-70 %	80-85 %	> 88-92 %	>70 %
BOD_5	85- > 90 %	> 90 %	> 90 %	> 90 %
Colour	40-50 %	70-85 %	> 80 %	> 80 %
Comments				SS = 0%

Table 3.2. Current performance of biological treatments

Ozonation

With ozonation, and an ozone dose from 5-30 mg/L up to 90-100% of residual colour can be removed. However for certain more stable dyes, larger doses of ozone (>70 mg/L) could be necessary and that would increase total costs. Concerning treatment of COD ("strong COD") ozone is less effective with only 15% removal. With this ozonation technique 30-80% of the water could be reused in textile processing depending on the required water quality.

Basically, the main advantages of ozonation are: efficient treatment of most dyes; complementary action on residual COD, e.g. total or partial destruction of detergents; deodorisation, and disinfection effects; no sludge production; water recycle (30-80 %) depending upon use and textile process requirements.

The main disadvantages are:

- investment costs are often too high for textile SMEs,
- a few dyes are more resistant to treatment and necessitate high ozone doses (> 70 ppm),
- ozone has a limited effect on COD removal (15 %),
- there is no effect on salinity (that could be a disadvantage if water has to be recycled in some dyeing process).

The associated costs, following the ozone equipment demand (air or oxygen), for a standard effluent with an overall flow of 100 m^3/day, are between 0.1-0.2 €/m^3.

Numerous published articles express the benefits of combining with UV/H_2O_2 to increase the efficiency of ozone. Most of these articles relate to laboratory scale experiments. In general, the addition of UV and/or H_2O_2 slightly increases the purification. But because of the associated costs, this additional step is not really justified.

III.3.3.3. Textile sectors concerned

Finishing mills (dyeing and printing).

III.3.3.4. Level of industrialisation

- biological activated sludge (current),
- biological anaerobic system (rare),
- bacterial beds, lagoons (rare),
- biological activated sludge + physico-chemical (common),
- membrane bioreactor (less common, mostly used for limited volumes <500 m^3/day),
- biological + ozone (less common, in development when water price is high and water recycling is recommended),
- biological + powdered active carbon or a polymer coagulant with good efficient colour removal (less common),
- biological activated sludge + membranes (less common, in development when water price is high and water recycling is recommended).

The combination of the biological activated sludge process, sand filtration, and ozonation for textile waste-water treatment and reuse can be considered a conventional technology, since many firms have already applied it on an industrial scale in the past few years. However, the suitability of this technology for purification of textile effluents has to be verified for each case considering both the technical and economic issues. The proper operating conditions, especially regarding ozone dose, have first to be evaluated on a laboratory and pilot scale before the realisation of an industrial plant.

III.3.3.5. Economic data

Note: As noted above it is very difficult to give real and representative data so the following figures must just be considered as indicative.

For treating 1000 m^3/day of effluent:

biological activated sludge: capital costs: 800 K€-1M€; operating costs: 0.2-0.3 €/m^3.

III.3.3.6. Combination possibilities

This technique can be used in combination with other treatments such as chemical-physical, and tertiary treatments such as ozone, membranes, activated carbon, chemical, etc.

Activated sludge combined with membranes represents a promising method to remove colour and reduce the organic content. In the same way a membrane filtration step could successfully be added to physical-chemical waste-water treatment. The use of highly selective membrane processes, such as nanofiltration (NF) and reverse osmosis (RO), allows the reuse of clean colourless textile waste-waters that provides direct environmental and economic benefits. Different membrane systems could be recommended but NF and RO offer the best guarantees.

Biological activated sludge is considered by the BREF document[1] as a BAT.

III.3.4. Separation techniques

This involves several techniques of which the most developed and used are the *membrane techniques* involving filtration (separation of suspended molecules or dissolved substances).

Note: *Further information on membrane processes see Section 3.*

Membrane filtration could be applied at different stage or steps in the flow-sheet:

- on raw effluent, mostly on a specific effluent for concentration and/or recycle of chemicals or products,
- on treated effluent, as a polishing technique to obtain high levels of quality or to recycle water (it could successfully be added to physical-chemical or biological waste-water treatment).

Activated sludge combined with membranes represents a promising process to remove colour and reduce organic content.

The use of highly selective membranes, such as NF and RO, allows textile waste-water for reuse thus achieving direct environmental and economic benefits.

With these membranes techniques, two points should be very carefully considered:

- pre-treatment filtration step (e.g. MF and/or UF) to prevent or limit clogging and fouling problems,
- re-use or destruction of the concentrated retentate.

Nano-filtration[10] separates low molecular weight molecules and some divalent salts giving an appreciable softening effect on the water. The resulting permeate quality is good enough for reuse in rinsing or some washing operations.

Reverse osmosis, because of complete removal of salinity, allows total use of the permeate, but due to high working pressures the energy costs are significant. This represents a disadvantage, and limits use on an industrial scale.

From an economic point of view, waste-water reuse is particularly attractive for textile industries. In some cases, the fresh water used in production could be purchased at a high price (0.8 € to >2 €/m^3).

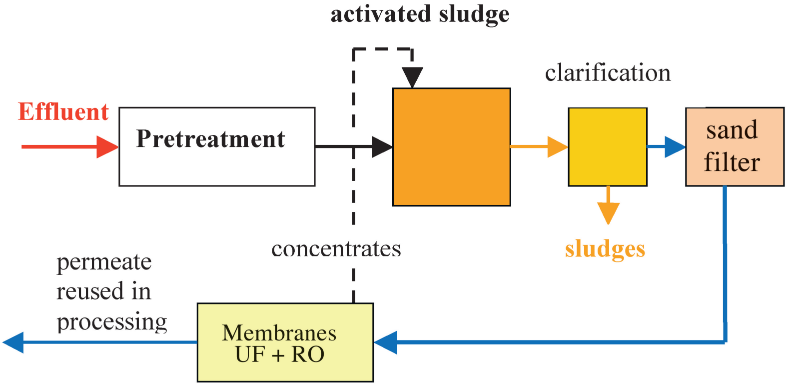


Figure 3.4. Example of combination of techniques using membranes

For a textile mill which produces 1000 m^3/day the total waste-water treatment costs (investment, energy and consumables) applicable to the membrane finishing step are between 0.5 to 0.8 €/m^3 *(these average values are indicative and should not be extrapolated to all textile mills. They are strongly dependent of the type and the characteristics of the membranes and the composition of the effluent).*

The global cost integrating the complete waste-water treatment chain is between 2-4 €/m^3.

Among other separation techniques, adsorbents such as **activated carbon** could also be used as polishing treatment for purification. But its associated costs, including regeneration and replacement, are relatively high and limit its use on a large industrial scale. In some cases, activated carbon could be directly used either in activated sludge or in the flocculation step to increase depuration yield. However again high costs and high treatment volumes limit this application.

III.3.5. Advanced Oxidising and Degradation Techniques

III.3.5.1. Ozone

Ozone treatment is currently one of the most efficient techniques for decolouration. Its oxidising power has been demonstrated on the majority of organic chemicals used in textile industry and is currently used at industrial scale.

This treatment is generally recommended as a tertiary treatment downstream of biological activated sludge, after sand filtration.

Basically, the main advantages of ozonization are: efficient degradation of most dyes; complementary action on residual COD (total or partial destruction of detergents); deodorisation, and disinfection effects; no sludge production; water recycling (30-80% depending upon uses and textile process requirements).

As regards the main disadvantages: high investment costs for textile SMEs, few dyes are more resistant and thus require high ozone doses (> 70 ppm), limited effect on COD removal (15%).

The use of ozonation techniques is described in the section on combination of biological sludge and ozonation (III.3.6.1.).

A wide variety of advanced oxidation processes are available[4,16] for waste-water treatment. Among these, photocatalytic processes are the most promising as they are reputed to complete the degradation initiated by biological treatment. Of such technologies the Photo-Fenton reaction is identified as having the most promise. Solar irradiation combined with a photo-catalyst,[14] such as TiO_2, could represent an economic alternative for sunny countries where the discharge regulations are not too restrictive.

III.3.5.2. Photocatalysis, Solar application, UV treatment, Fenton reaction

a) General principles

(Detailed discussion of the principles of these systems is given in Section 3).

A wide variety of advanced oxidation processes[6] are available for waste-water treatment based on the catalytic production of hydroxyl radicals by systems such as: TiO_2/UV, Fe/UV-Visible, and the photolysis of hydrogen peroxide or ozone using: H_2O_2/UV, O_3/UV and H_2O_2 /O_3/UV.

They are used to complete the degradation initiated by biological treatment or as a pre-treatment to enhance the biodegradability of waste-water containing recalcitrant or treatment-inhibiting compounds, by creating intermediate reaction products can be degraded more readily by micro-organisms in a biological post-treatment.

b) General performance

In general both Photo-Fenton (Fe/UV-visible) and TiO_2 photocatalysis give excellent results especially on waste-waters that contained organic compounds (toxicity, colour, etc). In specific cases high COD and BOD removals are found (90-95 %), especially in the removal of colour.

c) Textile sectors concerned

Waste-water containing non-biodegradable dyes.

The technology has its main applications in industrial waste-water treatment especially for problem effluents that are non-biodegradable or difficult to treat by other conventional treatment processes.

d) Level of industrialisation

The technology has recently been demonstrated with the first commercial application by CIEMAT. Therefore it is seen to be a strongly emerging technology with a high potential for a wide range of industrial waste-waters contaminated by organics.

The technology is at an emergent level, with TiO_2 photo-catalysis[14] at the level of a demonstration plant and Photo-Fenton[11] at commercial level but to date only one plant has been installed (Summer 2004).

e) Economic data

Because of the limited commercial experience not much data has been published. Nevertheless from CIEMAT and DLR experience a few operating data are available:

- TiO_2: waste-water containing 300 mg/L COD (i.e. 100 mg/L TOC) 18 €/m^3,
- Photo-Fenton: waste-water containing 300 mg/L COD (i.e. 100 mg/L TOC) 9.5 €/m^3,
- These costs are calculated for more than 90% COD reduction,
- UV plant total costs are estimated to between 1-5 €/m^3 (depending the volume to be treated).

Photocatalysis used as a pre-treatment for the enhancement of the biodegradability of waste-water will be cheaper but a case-by-case study will be necessary before implementation.

This technology is a potential alternative to established technologies for industrial waste-water treatment. The feedback from the textile industry, as well as from potential producers of the plants is very positive. Nevertheless more demonstration plants are necessary to show the industrial feasibility of the technology. Therefore integration of photo-catalytic water detoxification into the control and monitoring system of textile plants will be developed and demonstrated in the project InProTex funded by the German Ministry for Education and Research. Positive feedbacks have also been given by chipboard producers and the paper industry as well as chemical and waste disposal industries (see report from Paper cluster).

f) Main advantages and limits of the technique

The main advantage of the technique is its applicability to nearly every waste-water problem caused by organic pollution. Even toxic substances like hydrazine or polymers like lignin can be treated. To use the technology most efficiently the waste-water should be of a certain composition and include the required chemicals like photocatalysts or oxidising agents. In addition a suitable source of photo-energy is required. These parameters are crucial to achieve optimised cost effectiveness.

The technique can be widely used in textile industry especially for decolouration, but also to reduce substances like oils or other additives that cannot be treated by biological processing. Limits might be reached for municipal waste-water because this normally has a variable composition and does not normally contain substances that cannot be handled by cheaper biological treatment.

g) Examples of use in combination with other waste-water treatments

This technique could be used (for reducing costs) in combination with other conventional treatment such as:

- biological treatment,
- physical-chemical treatment.

h) State of development, level of industrialisation (laboratory, close to industrial commercialisation)

Although a very large number of articles have been published the technology is still not established for commercial waste-water treatment.

i) Comments - BREF Textile document and BAT

Photo-Fenton and photocatalysis are mentioned as techniques that could be used to degrade colour and organic recalcitrant chemicals.

III.3.6. Combination of techniques

III.3.6.1. Combination of biological activated sludge process and ozonation

a) General principles: Short description of the technique

Aerobic biological processes allow the removal of suspended and dissolved organic substances in waste-water, exploiting the bio-absorbance and metabolic transformation processes of colonies of micro-organisms that develop in a controlled way under aerobic conditions.

As a result of these processes, the suspended and dissolved organic substances are partly mineralised and partly transformed into settleable solids that can be removed by gravity. Therefore, the treatment consists of two phases: the first aeration and the second settling. In the biological activated sludge process, the aeration phase is obtained by a suspended biomass, in which the bacterial mass is dispersed in the liquid to be treated and continuously mixed by aeration. The bacterial mass and the waste-water constitute the so-called mixed liquor.

The biological activated sludge process may be applied each time a bio-oxidative process is required: the process is classified according to the particular phase of the metabolic mechanisms that presides over it, i.e. aerobic or anaerobic, and/or the flux scheme, e.g. differentiated aeration; complete mixing; contact and stabilisation plants.

During the bio-oxidative process the non-settleable suspended solids and the dissolved solids are transformed into a sludge; which is extracted from the bottom of the settling tank to be sent to the sludge treatment plant or, according to other schemes, removed directly from the aeration tank. A part of the sludge is recirculated in the aeration tank to achieve the appropriate treatment the aeration tank, (so-called "sludge age") to complete the bio-oxidative processes. Furthermore, the extracted sludge recirculation allows reduction of the volume of the aeration tank, since the hydraulic retention time in the latter is much lower than the age of the activated sludge inside the tank.

The biological activated sludge process removes the majority of the Biological Oxygen Demand (BOD) and suspended solids found in waste-waters. However, in an increasing number of cases this level of treatment has proved to be insufficient to provide reusable water for industrial recycle. Thus, additional treatment steps have been added to waste-water treatment plants to produce an effluent of higher quality, the so-called tertiary treatments.

Ozonation[15] has been found to be a suitable tertiary treatment that can be applied downstream to a biological activated sludge process for textile waste-water reuse. Water purification does not use pure ozone, but ozonized air, that is air in which part of gaseous oxygen content has been converted in ozone by means of an electrical discharge. The ozone can be produced both from dried air and from liquid oxygen.

Ozone oxidation has found several applications especially in drinking water disinfection, as a result of its capacity for rapidly destroying bacteria and its efficacy as regards viruses. The disinfecting action depends on the dissociation reaction $O_3 \rightarrow O_2 + O$, which occurs rapidly after ozone production, because O_3 is a very unstable gas. The reaction produces two oxidising agents, O_2 and O. The latter has a really high oxidising capacity, so it is able to break down many complex organic molecules into simpler molecules, so that refractory pollutants often become biodegradable substances.

The key process control parameters for ozonation are: ozone dose, contact time, and mixing. Ozone and waste-water are mixed in contact or reaction vessels and agitated by mechanical mixers, static mixers, diffusers, injectors, or in packed or bubble columns to optimise the dissolution of the gas. Membrane contactors have also been studied to achieve high gas transfer rates into the water. To reduce the cost of ozone oxidation, sand filtration is commonly used as a pre-treatment to remove suspended solids which could cause excess ozone consumption and clog the diffusers.

The combination of the biological activated sludge process, sand filtration, and ozonation for textile waste-water treatment and reuse can be considered a conventional technology, since many firms have already applied it on an industrial scale over the past few years. However, the suitability of this technology for purification of textile effluents still has to be verified for each case with consideration of both technical and economic issues. The proper operating conditions, with special regard to the ozone dose, have to be evaluated first on a laboratory and pilot scale before the realisation of an industrial plant.

b) General performance

A recent industrial-scale application of the biological activated sludge process followed by sand filtration and ozonation for textile waste-water reuse at an Italian firm has been described.[13]

The biological activated sludge plant described in the paper treats 2,000 m^3/day of waste-water from a dyeing and finishing plant; with the sand filtration and ozonation tertiary plant treating 1,000 m^3/day of secondary effluent, the rest being discharged to the public sewer. The operating conditions of the ozonation plant are: ozone dose: 45 g/m^3; contact time: 30 minutes with ozone/water mixing achieved by bubble columns.

Under the above conditions, the tertiary treatment allows: removal of about 40% COD from the secondary effluent; 35-50% non-ionic and anionic surfactant removal; 99% colour removal, based on the integral of the absorbance curve in the overall visible range; and around 85% removal of Total Suspended Solids (TSS).

This tertiary treatment does not affect the salt content of the secondary effluent with no observed changes in hardness, conductivity and chloride content of the waste-water compared to the values of the biologically-treated water. Total reuse of the tertiary effluents in the dyeing and finishing processes is also described in the paper. Comparison with the results obtained with softened water, showed that satisfactory results were obtained with 100% of the tertiary effluent in the dyeing of wool fibres and fabrics by acid dyes. However, dyeing of cotton is reported to be more problematic; a possible reason being that this kind of dyeing used direct dyes, that are not stable to hard water (hardness of the ozonized water: 48°F) and have poor chlorine fastness. Fulling is another finishing process that was successfully carried out the case-study with 100% ozonized water, as this process is not influenced by the hardness of the recycled water. The economic analysis of this study has shown that the operating costs of the ozonation process are about 0.10 €/m^3 of treated water, considering a water feed of 1,000 m^3/day to the ozonation plant and 220 working days/year.

Overall assessment of the treatment:

Biological activated sludge process:

Main advantages of the technique are:

- high removal of BOD_5 (85-95%),
- high removal of suspended solids (75-85%).

Main limits of the technique:

- poor decolourisation (20-30%, determined as absorbance at 420 nm),
- possible sludge bulking,
- possible foaming.

Ozonation:

Main advantages of the technique are:

- high level of decolourisation (80-90%) with ozone dose of 40 g/m^3 and contact time of 15-30 minutes (on treating effluent of a biological activated sludge process,
- high level of odour removal,
- short contact time 10-30 minutes usually sufficient for a good quality effluent.

Main limitations of the technique:

- partial COD removal 40% with an ozone dose of 40 g/m^3 and contact time of 15 minutes (on treating effluent from a biological activated sludge process), unless using high ozone doses,
- no effect on salt content,
- capital and operating costs can be relatively high, especially for waste-waters with high levels of SS, BOD, COD, or Total Organic Carbon (TOC) requiring high ozone doses.

c) Textile sectors concerned

Finishing mills (dyeing and printing).

d) Level of industrialisation

This combination is becoming more and more common. The combination of a biological activated sludge process with ozonation tertiary treatment is on a commercial level; however, as mentioned above, laboratory and pilot-scale studies are needed before installation to determine the proper operating conditions and to verify the cost-effectiveness.

e) Economic data

As mentioned above in part b, an economic analysis of this technology on an industrial scale at an Italian firm has shown that the operating costs of the ozonation process are about 0.10 €/m^3 of treated water on the basis of a water feed of 1,000 m^3/day to the ozonation plant and 220 working days/year. The capital cost for the tertiary plant in this case-study was about 600 K€.

f) Examples of use in combination with other waste-water treatments

The use of ozonation in combination with other treatment processes such as ultrasound, activated carbon, ion exchange, UV radiation, or hydrogen peroxide has been studied for the treatment of textile waste-water.[12]

The combination of the activated sludge process with chemical oxidation using ozone/UV radiation for reuse of textile waste-water has been reported.[12, 13, 15] It was found that, after the biological treatment, the combination of UV irradiation with ozone leads to a significantly higher COD removal compared to ozonation alone. The same authors have also reported the use of ozonation on biologically treated textile waste-water as a pre-treatment to nanofiltration.

It has to be mentioned that the combination of ozonation followed by the biological activated sludge process to improve the biodegradability of highly polluted wastes has also been studied for textile waste-water treatment and for other kinds of waste-waters. No industrial-scale application of ozonation followed by the biological activated sludge process aimed at textile waste-water reuse is known to the author.

III.3.6.2. Combination of biological activated sludge process and membrane filtration[15]

a) General principles: Short description of the technique

(More detailed information on the principles, equipment and operation of membrane processes see Section 3).[5]

Membrane filtration processes are separation methods at a molecular level that use a membrane, consisting of a thin film, as the filter medium.

There are two possible types of configuration for filtration:

- dead-end filtration, in which the solution to be filtered flows perpendicularly to the filtration medium; so that all the fluid passes through the filter that retains the solids contained in the liquid,
- cross-flow filtration, where the solution to be filtered flows parallel to the filtering surface and only a part of the fluid passes through the filter.

Whilst conventional filtration methods, such as sand filtration, are normally used in the dead-end configuration, membrane filtration processes most commonly use the cross-flow scheme. The reason is that the cross-flow configuration seems to be better at preventing membrane clogging, and therefore allows the membrane to be better protected. This is important because membranes are expensive and delicate materials that would not resist frequent chemical washings at ambient or hot temperature necessary to restore the initial filtration efficiency following membrane clogging.

The dimensions and characteristics of the particles to be separated determine the type of filtration process, conventional or membrane. When the particles have a dimension bigger than 50 µm efficient removal is possible with a conventional filtration process; however to remove mono- and di-valent salts or soluble polymers a membrane filtration process is required.

The main role of a membrane is to act as a selective barrier, allowing some components of the mixture to be treated to pass through and retaining other components. Therefore, there is only one stream that enters the membrane, the feed, while two streams exit from the membrane: the *permeate* and the *concentrate* (*retentate*). The permeate is the portion of the fluid that has passed through the semi-permeable membrane, whereas the concentrate stream contains the constituents that have been rejected by the membrane.

Each membrane process is characterised by the use of a specific kind of membrane that is able to transport one component faster than others, as a result of differences in the physical and chemical properties of the membrane and the species that cross it under the action of a driving force. This driving force acting on the single components of the feed can be: pressure difference; concentration difference; temperature difference; or an electro-driving force.

The membrane processes most commonly used in industrial waste-water treatment are those regulated by a pressure difference. Four such membrane filtration processes exist differing in the size range of particles being retained:

- ***microfiltration (MF),*** with a filtration range of 0.1-10µm, that allows removal of suspended solids, bacteria and other small organisms,
- ***ultrafiltration (UF),*** with a filtration range of 0.005-0.05µm (50-500Å), removing colloids, viruses and some organic molecules that have a molecular weight of 1-1000 kDa, determined by the Molecular Weight Cut-off (MWCO) of the membrane, i.e. the smallest molecular weight species for which membrane has > 90% rejection,
- ***nanofiltration (NF),*** with a filtration range of 0.0005-0.005µm (5-50 Å), that allows removal of sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 500 Da,
- ***reverse osmosis (RO)***, with a filtration range of 0.0001-0.001 µm (1-10 Å), that allows removal of monovalent salts and metal ions.

b) Performance: main advantages and limits of the technique

Biological activated sludge process:

Main advantages of the technique are:

- high removal of BOD_5 (85-95%),
- high removal of suspended solids (75-85%).

Main limitations of the technique:

- poor decolourisation (20-30%, colour determined by absorbance: 420 nm),
- possible sludge bulking,
- possible foaming.

Membrane filtration processes:

Main advantages of the technique are:

- excellent removal of salts when using NF or RO,
- excellent decolourisation when using NF or RO,
- excellent removal of solids when using MF or UF.

Main limits of the technique:

- susceptibility to clogging, that:
  requires chemical washing, with interruption of the treatment cycle,
  limits the membrane life requiring expensive membrane replacement.
- need to operate at high pressure especially with NF or RO,
- high operating costs,
- disposal of resulting concentrate (retentate).

It is important to remember that three factors have to be considered for the selection of the most advantageous membrane for a purification treatment:

- pore size of the membrane, that determines to a large extent what substances permeate the membrane and what substances are retained,
- membrane material, which determines the chemical resistance, susceptibility to fouling and thus suitability for various separations,
- membrane shape e.g. sheet, tubular, spiral wound, hollow fibre, because this determines the type of equipment, susceptibility to clogging, cleaning efficiency and any required pre-treatment.

When combined with NF or RO membranes the normal results of biological treatment are dramatically increased with total decolouration, COD and BOD removal all at levels > 90-95 %.

The main remaining problems are:

- high investment (membrane price) - large areas required due to slow flows and large waste-water volume,
- management of the concentrate - volume, toxicity, disposal costs,
- salinity which could represent some problems for several textile process.

Several studies have shown that, when using an NF or RO membrane as tertiary treatment of textile waste-water for reuse, removal of fine suspended solids and colloids from the secondary effluents is necessary to prevent fouling and damage to the membrane module by clogging. Hence, the use of effective pre-treatments downstream of a biological activated sludge plant, such as sand filtration, activated carbon adsorption, flocculation, flotation or other membrane processes (e.g. microfiltration or ultrafiltration), is fundamental to extend the life of NF/RO membranes, and consequently decrease the costs related to the membrane replacement. Ozonation has also been studied as a pre-treatment to the nanofiltration of biologically treated textile effluents to prevent membranes from fouling and to oxidize organic compounds that could affect the membrane behaviour

c) Main sectors concerned

Pressure-driven membrane filtration has been selected for the treatment and reuse of textile effluents mainly from dyeing processes, since they have the potential to either remove the dyestuff and allow reuse of the auxiliary chemicals used for dyeing, or to concentrate the dyestuffs and auxiliaries and produce purified water.

d) level of industrialisation

The combination of the biological activated sludge process, sand filtration and pressure-driven membrane filtration processes for textile waste-water treatment and reuse can be considered a *promising technology*.

In fact, from a technical point of view the application of pressure-driven membrane processes downstream of an activated sludge plant for textile waste-water treatment and reuse has been proved effective. This kind of application has however been mainly restricted to studies on a laboratory and pilot scale because of the high capital and operating costs involved. This combination could be justified if water recycling is the main objective especially if the price of fresh water is high (>1.5-3 €/m^3).

The combination of the biological activated sludge process with a pressure-driven membrane filtration[15] system is close to industrialisation. Several research works[2,9,12,15] have shown that this combination may allow water reuse in textile processes. However, in order to define the most effective approach on the technical and economical point of view in a case study, both laboratory and pilot-scale experiments are needed to determine:

- the most suitable membrane, which can guarantee the production of a permeate with the desired quality with minimised risk of clogging,
- the eventual need of a pre-treatment for the membrane process, to be applied downstream the biological plant,
- the optimum conditions for the operation of the tertiary plant and the recovery rate that can be obtained.

e) Economical and technical feedback

Microfiltration (MF) is suitable to remove colloidal dyes from the exhausted dye-bath and subsequent rinses with the auxiliary chemicals remaining in the permeate. Hence, MF can seldom be used as the only membrane process to be applied on a biologically treated textile waste-water to allow water reuse, but it has been successfully applied on a small scale as a pre-treatment to nanofiltration to prevent membrane fouling.

Ultrafiltration (UF) has been studied as a single step treatment of secondary textile waste-water. The permeate obtained was of appropriate quality to allow reuse of the waste-water in minor operations (rinsing, washing), but it did not have the requirements to be reused in delicate processes such as dyeing yarns with light colours UF has also been successfully applied on a pilot scale as pre-treatment to either nanofiltration or reverse osmosis.

Nanofiltration (NF), as mentioned above, has been successfully applied as treatment of secondary textile effluents after MF.

A pilot-scale study on the application of sand filtration, MF, and NF in series as a tertiary treatment system for textile waste-water has shown that:

- the use of sand filtration and MF is fundamental to the reduction of suspended solids (100%) and turbidity (78%),
- COD is removed partially by sand filtration and MF (30%) and totally after NF,
- colour, one of the most important parameters in checking textile waste-water quality for reuse, is removed almost completely by NF (81%).

Hence, the NF permeate after these processes was suitable for reuse.

Reverse osmosis (RO) is suitable for removing ions and larger species from dye-bath effluents. The permeate produced is usually colourless and low in total dissolved solids.

A pilot-scale study on the application of sand filtration, UF, and RO in series as tertiary treatment system of textile waste-water showed that:

- COD is removed partially by sand filtration and UF (52%), and totally after RO,
- sand filtration and UF enable high removal of turbidity (92%) and total suspended solids (96%),
- sand filtration and UF have only a slight effect on colour removal, but RO provides very good removal (90%).

Some dyeing tests carried out within this pilot-scale study, demonstrated that the RO permeate can be reused in all dyeing processes, even the most demanding of water quality (dyeing in light shades).

An economic analysis within a pilot-scale study in which sand filtration, MF, and NF (both using spiral-wound membranes) were applied as a tertiary treatment system of textile waste-water from an activated sludge plant has shown that the operating costs would be about 0.34 €/m^3, with a payback of the investment costs of about 3 years.

According to the results of another pilot-scale study, in which sand filtration, UF, and RO (again both with spiral-wound membranes) were applied as the tertiary treatment, the operating and investment costs, depreciated in 10 years, would be about 0.97 €/m^3; of which energy consumption contributes most (34%) of the total costs.

It is clear that, to minimise the costs of a tertiary treatment system in which two different membrane processes are applied in series, MF should be preferred to UF as the first membrane process and NF should be preferred to RO as second process, provided that this is allowed by the quality of the incoming waste-water, because MF and NF operate at lower pressures than UF and RO, respectively, and therefore have a lower energy consumption.

III.3.7. Evaporation techniques

(Further details of the principles, equipment and operating procedures see Section 3).[3]

Evaporation process can be performed through different techniques like falling film evaporation (FFE), multi-effect distillation (MED) and thermo-vapour compression (TVC). In the last few years a lot of efforts were performed in order to test solar evaporation process. Presently evaporators are mainly used for the treatment of effluents from landfill leachate, plating, and food processing.

Evaporation is generally not used extensively in the textile industry. Some applications that have been examined are the treatment of effluents from wool washing and combing (high COD and low volumes in comparison to current finishing mill). These effluents are treated by thermo-vapor compression (TVC).

In the case of dyeing effluents, evaporation (TVC) could provide a distillate with low COD and approaching total colour removal, but there are major technical disadvantages with:

- expensive costs for high volumes of waste-water (energy consumption, the volume of the concentrate and costs of disposal: >120-150 €/t),
- high pollution load in the concentrates,

- and potential contamination of the distillate preventing reuse (due to presence of some VOC or hydrocarbons in the waste-water),
- scaling of the boiler and heat exchanger surfaces.

The evaporation technology faces serious problems when treating hard polluted waste-water (as the concentrated solutions) cause of the scaling processes on the heat exchanger surfaces. Some companies are seeking development of innovative or improved evaporation plant which is able to reduce scaling process and operating costs.

So basically, the main commercial applications of evaporation are:

- wool scouring (washing)*,
- cotton mercerising (recovery of the NaOH solution used in the mercerisation† of cotton fabrics).

** Raw (greasy) wool contains substantial amounts of natural pollutants (about 40% by weight) that must be washed off (scoured) before the wool can be used in the textile processes. The major contaminants are wool wax (solvent-extractable) and dirt (water-soluble). Most of these contaminants are discharged from the wool scour as aqueous effluent.*

† Mercerisation is a continuous chemical process used for cotton/polyester goods to increase hydrophilicity, dye-ability, lustre, and appearance. During mercerising, the fabric is passed through a cold solution of caustic soda (30% caustic). About 3% of the caustic is present in the wash water from the first treatment. At this stage this solution is too dilute and evaporation allows the recovery of dilute NaOH solutions for recycle in the production process.

Typical composition of scouring waste streams are given in the following table:

Contaminant (mg/L)	*Grease*	*Strong flow*	*Rinse-water*
BOD	*4000*	*9800*	*300*
Suspended solids	*4500*	*14600*	*800*

Outlook

In the last few decades new effluent treatment systems have been designed to reduce aqueous discharges to a minimum. These systems seek to separate water from contaminants to produce two streams. One is a concentrate containing most of the contaminants, the other is a stream containing low contaminant levels that is suitable for recycling in the scouring line. Most of the systems involve an evaporation step although the use of membranes has been reported in some instances. Because of higher thermal efficiencies, multi-effect evaporation systems are used to evaporate scouring effluents.

A major disadvantage with evaporation by itself is that the resulting concentrates contains all the contaminants: e.g. wool wax, grease, and dirt.

This could represent some problems for the sludge disposal (in some case incineration is required).

Currently scouring and mercerising, seem to be the only uses of evaporation in wet textile processing. These techniques could also be used in combination with membrane techniques to reduce the concentrates and limit disposal costs (few current industrial realisations).

The technology is expensive so the treatment of large amount of waste-water is not economically conceivable even if the thermal energy is recovered during evaporation.

Some studies of the technical and economic feasibility of evaporation to treat specific streams of textile waste-waters have been made, but the textile sector is economically poor and there are not many incentives to try new systems.

In spite of this some companies have developed innovative or improved evaporation plants which are able to avoid problems of scaling and reduce operating costs with the aim of recovering the distilled water and related energy. Maybe with such new developments and if the volumes of concentrates and their disposal costs can be reduced, then evaporation may feature in the treatment of textile waste-waters in the future.

III.4. SYNOPSIS OF BREF DOCUMENT: BAT FOR WASTE-WATER TREATMENT

Waste-water treatment follows at least **three different strategies**:

- central treatment in a biological waste-water treatment plant on site,
- central treatment off site in a municipal waste-water treatment plant,
- decentralised treatment on- or off-site of selected, segregated single waste-water streams.

All three strategies are BAT options when properly applied to an actual waste-water situation. Well-accepted general principles for waste-water management and treatment include:

- characterising the different waste-water streams arising from the process,
- segregating the effluents at source according to the type of contaminant and load before any mixing with other effluents. This ensures that a treatment facility receives only those pollutants for which it is designed. Moreover, it enables the application of recycling or re-use options for the treated effluent,
- allocating contaminated waste-water streams to the most appropriate treatment,
- avoiding the introduction of waste-water components into biological treatment systems when they could cause malfunction of such a system,
- treating waste streams containing a relevant non-biodegradable fraction by appropriate techniques before, or instead of, a final biological treatment.

According to this approach, the following techniques are determined as general *BAT for the treatment of waste-water from the textile finishing and carpet industries:*

- treatment of waste-water in an activated sludge system at low nutrient-to-micro-organism ratio, under the prerequisite that concentrated streams containing non-biodegradable compounds are pre-treated separately,
- pre-treatment of highly-loaded (COD >5000 mg/L) selected and segregated single waste-water streams containing non-biodegradable compounds by chemical oxidation. Such waste-water streams are padding liquors from semi-continuous or continuous dyeing and finishing; desizing baths; printing pastes; residues from carpet backing; exhausted dyeing and finishing baths.

Certain specific process residues, such as residual printing pastes, and residual padding liquors are very strongly contaminated and, where practicable, should be kept out of waste-water streams. These residues should be disposed of by appropriate technologies, for example thermal oxidation because of the high calorific value of such wastes. For the specific cases of waste-water containing pigmented printing paste or latex from carpet backing, precipitation/flocculation and incineration of the resulting sludge is a viable alternative to chemical oxidation. For azo-dyes, anaerobic treatment of padding liquor and printing pastes before a subsequent aerobic treatment can be effective for colour removal.

If concentrated effluent streams containing non-biodegradable compounds cannot be treated separately, additional physical-chemical treatments would be required to achieve equivalent overall performance. These include:

- tertiary treatments following the biological treatment process. For example adsorption on activated carbon with recycling of the activated carbon to the activated sludge system; followed by destruction of the adsorbed non-biodegradable compounds by incineration, or treatment of the excess sludge, biomass with spent active carbon, with free-radical oxidation processes generating OH^*, O_2^{*-}, CO_2^{*-},
- combined biological, physical and chemical treatments with the addition of powdered activated carbon and iron salts to the activated sludge system and reactivation of the excess sludge by “wet oxidation” or “wet peroxidation”, if hydrogen peroxide is used,
- ozonation of recalcitrant compounds prior to the activated sludge system.

For effluent treatment from the wool scouring sector (water-based process) BAT is to:

- combine the use of dirt removal / grease recovery loops with evaporative effluent treatment, integrated incineration of the resulting sludge and full recycling of water and energy for: new installations; existing installations with no on-site effluent treatment; installations seeking to replace life-expired effluent treatment plant,
- use coagulation/flocculation treatment in existing mills where it is already in use in conjunction with discharge to a sewerage system employing aerobic biological treatment.

Whether or not biological treatment can be considered as BAT must remain an open question until better information on its costs and performance can be assembled.

SLUDGE DISPOSAL

(see also Paper cluster report in Section 2.I.).[6]

For sludge from waste-water treatment of wool scouring effluent.

BAT is to:

- use sludge in brick-making or adopt any other appropriate recycling routes,
- incinerate the sludge with heat recovery, provided that measures are taken to control emissions of SO_x, NO_x and dust and to avoid emissions of dioxins and furans from organically bound chlorine based pesticides potentially contained in the sludge.

III.5. EMERGENT AND PROMISING TECHNIQUES

III.5.1. Emergent techniques listed in the BREF document

Emerging techniques included in the BREF mainly concern reducing the pollution impact and energy consumption from the finishing or printing technologies:

- use of enzymes which as biocatalysts activate and accelerate some chemical reactions e.g. desizing, scouring, bleaching, bio-polishing,
- plasma technology for degreasing, desizing, functionalisation treatment*, etc.,
- electron beams for functionalisation treatment**, polymerisation, etc.,
- supercritical CO_2 in some dyeing processes,
- ultrasonic treatment for dispersion of dyestuffs, emulsification,
- electrochemical dyeing, vat and sulphur dyes: redox systems,
- alternative textile auxiliary reagents: complexing agents, chemical less toxic and readily biodegradable compounds,
- fuzzy logic for process control,
- on-line monitoring to reduce chemical and/or to limit water consumption.

(*) *creation of free radical groups by plasma treatment and grafting by chemical impregnation (liquid or reactive gas) to make new properties (water-proof, dyeing efficiency, crease resistant…).*
(**) *creation of free radical groups with electron beam treatment and grafting by chemical impregnation to make new properties (ion exchanger, antibacterial, water-proof, crease resistant, etc.).*

Two main examples of processes concerning water treatment:

- Advanced Oxidation processes: UV activated photolysis of hydrogen peroxide for colour removal combined with bio-flotation treatment,
- reed bed systems (phyto-purification): such systems could be used to purify or to complete the waste-water purification.

III.5.2. Emerging and promising techniques

Many techniques can and are currently used to treat textile waste-water effluents (overall effluents or specific bath end-of-pipe of dyeing machine). The analysis of the literature does not allow clear identification of new emergent techniques.

Nevertheless, the following techniques could be considered as promising for the future:

- advanced oxidation processes: UV activated photolysis of hydrogen peroxide for colour removal combined with bio-flotation treatment,
- reed bed systems (phyto-purification): such systems could be used to purify or complete waste-water purification,
- use of membranes in combination with activated sludges with trend to zero liquid waste on site,
- new generation of chemicals with high coagulant and/or oxidative properties (e.g: ferrates),
- catalytic ozonation to treat strong COD from highly bio-recalcitrant compounds (developed by the French company Technavox),
- several combinations of techniques such as membranes + activated sludges + evaporation (concentrates) could present some interesting techniques for the future.

The use of new automation systems (fuzzy control and neural networks) can present an opportunity for improving the efficiency of biological or physicochemical waste-water plants using modern methods of Computational Intelligence (CI). Most of the current developments concern municipal waste-water treatment plants (www.wincc.de) or the chemical industry (www.aspentech.com; www.passavant-intech.de).

III.6. CONCLUSION

For textile finishing SME, the ideal waste-water technique should be able, technically and economically, to treat high volumes, a large range of organic chemicals and be easy to manage.

Numerous publications describe experiments on textile effluents. Most of time, they are related to laboratory pilot studies, on synthetic effluents, mostly concerned with problems of colour.

Because of the specific nature of each mill, and the complexity of the treatment (different effluent composition, limiting discharge values, opportunity or necessity to recycle water), one technique could not reach the regulatory discharge limits.
Thus, many treatment techniques can be proposed (physical, chemical, biological) and can be considered as efficient. The most simple and the most efficient technique that can reach the current limiting discharge values is biological activated sludge.

Nevertheless, even a Textile SME has to reach high purification or water recycling objectives, so a tertiary or finishing treatment is generally required.

In order to allow significant or complete water recycling, the most promising configuration is: activated sludge + ozone or membrane filtration (NF, RO). Ozone and membranes are the most promising technologies and are the object of several developments at industrial scale. With new application in municipal waste-water treatment, new generation of membrane with lower prices and higher performances (flow, cleaning, life-time) are expected. They should offer new perspectives even for high volumes and represent a good compromise. In both cases, if an economic feedback could be demonstrated, especially by recycling a large quantity of water, these systems are promised a great future. One of the biggest difficulties consists in the management of the concentrates from the membranes.

As regards new perspectives many additional techniques, could be conceived. For example in photo-catalytic processes, we could imagine a new generation of enzymes, specific chemicals[16] that could offer new treatment opportunities, in increasing current purification yields on bio-recalcitrant molecules (dyes, hydrocarbons, detergents).

References

Most of the figures and commentaries are extracted from IFTH reports (Technical assistance, studies, R&D projects).

1. BREF textile, *Reference Document on Best Available Techniques for the Textile Industry*, European Commission, directorate-general Joint Research Centre, Institute for Prospective Technological Studies, Edificio Expo c/Inca Garcilaso s/n, E-41092 Seville, Spain, November 2002
2. M. Marcucci, G. Nosenzo, G. Capannellli, I. Ciabatti, D. Corrieri and G. Ciardelli, *Treatment and reuse of textile effluents based on new ultrafiltration and other membrane technologies*, Desalination **138**, 75-82, (2001)
3. A. Sungpet, R. Jiraratananon and P. Luangsowan, *Treatment of effluents from textile-rinsing operations by thermally stable nanofiltration membranes*, Desalination **160,** 75-81, (2004)
4. V. Augugliaro, C.Baiocchi, A.Bianco Prevot, E. Garcia-Lopez, V. Loddo, S. Malato, G. Marci, L. Palmisano, M. Pazzi and E. Pramauro, *Azo-dyes photocatalytic degradation in aqueous suspension of* TiO_2 *under solar irradiation*, Chemosphere **49**, 1223-1230, (2002)
5. A Bes-Pia, J.A. Mendoza-Roca, M.I. Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar, *Combination of physico-chemical treatment and nanofiltration to reuse wastewater of a printing, dyeing and finishing textile industry*, Desalination **157**, 73-80, (2003)
6. C. Sattler, J. Böttcher, K.-H. Funken, N. Monnerie, L. de Oliveira, R. Schäfer, H. Müller, T. Schäfer, S. Schulz and R. Stummer, *Integrated photocatalytic waste-water recycling in textile finishing*, CUTEC Serial Publication No.57, 3rd International Conference on Oxidation Technologies for Water and Waste-water Treatment - Special Topic: AOPs for Recycling and Reuse, pp 18-2, May 20032.
7. M. Marcucci, I. Ciabatti, A. Matteucci and G. Vernaglione, *Membrane technologies applied to textile wastewater treatment*, Ann. N. Y. Acad. Sci. **984,** 53-64, (2003)

References

8. J.F. Courtin, *Traitement biologique des effluents*, L'Industrie Textile n°1333, 51-52, (2001)
9. R. Martinetti and L. Sainctavit, *Dépollution par éléctrofloculation*, L'Industrie Textile, N°1288, 49-52, (1997)
10. R. Martinetti and L. Sainctavit, *Le recyclage de l'eau*, L'Industrie Textile, n°1301, 46-51, (1998)
11. S. Malato, J. Blanco, J. Caceres, A.R. Fernadez-Alba, A. Agüera and A. Rodriguez, *Photocatalytic treatment of water soluble pesticides by photo-Fenton and TiO2 using solar energy*, Catalysis Today **76**, 209-220, (2002)
12. M. Marcucci, G. Ciardelli, A. Matteucci, L. Ranieri and M. Russo, *Experimental campaigns on textile wastewater for reuse by means of different membrane processes*, Desalination, **149**(1), 137-143, (2002)
13. G. Ciardelli, L. Corsi and M. Marcucci, *Membrane separation for waste-water reuse in the textile industry*, Resources, Conservation and Recycling **31**, 189-197, (2000)
14. M. Kositzi, A. Antoniadis, I. Poulios, I. Kiridis and S. Malato, *Solar photocatalytic treatment of simulated dyestuff effluents*, Solar Energy, **77**, 591-600, (2004)
15. M. Marcucci, G. Ciardelli, I. Ciabatti and A. Bottino, *New approaches for the treatment and reuse of textiles effluents based on different membrane technologies.*
16. I. Ciabatti, L. Ranieri and M. Marcucci, *Application of a novel super-oxidant to purify carbonising water*, ILE Workshop L'Aquila, Italy, 2005.
17. R. Martinetti, *Waste-water treatment in textile industry: overview of available techniques*, ILE Workshop Madrid, Spain, 2004.

IV.

INDUSTRIAL LIQUID EFFLUENTS IN THE PLATING INDUSTRY

Cluster Leader

Protection des Métaux, France - J. Halut.

Members

Centre de Recherches pour l’Environnement l’Energie et le Déchet, Limay, France - I. Milo.

Ecole Nationale Supérieure des Mines de Saint-Etienne, France - P. Benaben.

Faculdade de Ciências do Porto, Portugal - F. Silva.

Institut National Polytechnique de Lorraine, Vandoeuvre, France - I. Gaballah.

Institute of Chemistry, Vilnius, Lithuania - O. Gyliene.

Katholieke Hogesschool Sint-Lieven, Gent, Belgium - R. De Ketelaere.

Enviroact, Wageningen, Netherlands - M. Janssen.

Lamik S.A, Zarautz, Spain - I. Acuña.

Led Italia, Pordenone, Italy - C. Del Piccolo.

Technical University of Lodz, Poland - Z. Kolacinski.

Université de Liège, Belgium - J. Frenay.

University of Roma, Italy - C. Lupi.

Venezia Tecnologie S.p.A, Venecia, Italy - L. Meregalli.

INDEX

IV.1. INTRODUCTION

The surface treatment industry in Europe employs more than 500,000 people[1] (source: EUROSTAT). Due to the type of materials and chemicals used, this industry is a source of water pollution, particularly by heavy metals which constitute 40% of total pollution by the industry[2] (French Ministry of the Environment), which can affect the health of the population.

The European IPPC Directive 96/61 concerning integrated pollution prevention and control (IPPC) has the following aims:

- to prevent or minimise air, water and soil pollution by emissions from industrial sectors, including surface treatments, with a view to achieving a high level of environmental protection, particularly in terms of neighbourhood pollution (noise, vibration), including measures concerning waste,
- and to limit the consumption of raw materials, water and energy.

The goal of this chapter is to demonstrate that the use of clean technologies to decontaminate liquid effluents from workshops concerned with surface processing of metals are not a dream but are already a reality in a certain number of companies.

IV.2. PROBLEMS ASSOCIATED WITH THE INDUSTRY

The surface treatment industry uses large quantities of chemical products, many of which are toxic to man and the environment. Such chemicals provide the major components in the gaseous, liquid, and solid effluents from the industry and represent 40% of the total aqueous metallic pollution produced by industry. Globally the industry produces 20% of the total aqueous pollution of which the surface treatment sector contributes 6 to 8%. This amount has been consistently reduced for some years thanks to the introduction of strict regulations concerning discharge levels and to the introduction of techniques to purify effluents.

IV.2.1. Rejects and wastes

Rejects are defined as materials emerging from an industry process excluding end products before any subsequent reprocessing or valorisation. Liquid and gaseous rejects, when they are more or less polluted at the exit of an industrial process are defined as effluents defined before any recovery processes.

In the surface treatment industry such effluents include treated liquid and gaseous rejects and not disposed into the natural habitat. Such solid or liquid rejects are sent either to agreed treatment centres or to disposal sites are termed liquid or solid wastes.

IV.2.2. Origin of wastes

The surface treatment industry uses large quantities of water in its processes. Water does not only feature in the composition of processing baths as, for example: degreasing, etching, or plating, but especially in the rinsing of the pieces between the different processes and in the final washing stage. During these different phases water is polluted by heavy metals and their salts and must be treated before disposal into the natural habitat according to very strict and specific standards in every country of the EC.

In addition these processing baths are often heated and the gaseous effluents that are emitted that must be washed before dispersal into the atmosphere to conform to the EC atmospheric pollution levels.

The different sources of potential pollution are:

- bath to bath transfer of the work piece,
- spillages, accidents, etc.,
- overflow, droplets falling from work-pieces,
- draining of the exhausted processing and rinsing baths,
- evaporation.

IV.2.3. Types of waste

Four categories of waste are produced by the surface treatment industry:

- solid wastes from decontaminating processes (mostly hydroxides muds): 47%,
- wastes from preparation and coatings: 36%,
- solvents: 7.6%,
- liquid mineral wastes: 9.4%.

Rejects from workshops are divided in two classes: concentrated flows and dilute flows:

- concentrated flows include solutions from the draining of exhausted baths, rinsing baths and gas scrubbers,
- dilute flows mainly of water from current rinsing baths and washing of floors.

IV.2.4. Nature of the pollutants contained in the surface treatment industry effluents

IV.2.4.1. Cations

These are generally the ions of heavy metals such as: aluminium, chromium, copper, iron, lead, magnesium, nickel, tin, and zinc, that are the most frequently rejected; also smaller quantities of noble metals: gold, palladium, rhodium, and silver; as well as the less common metals: molybdenum, titanium, or zirconium.

IV.2.4.2. Anions

The largest proportion comes from the metallic salts contained in the processing and etching baths. These are chlorides, cyanides, nitrates and nitrites, phosphates, sulfates, chromium in the anionic form as well as fluorides.

IV.2.4.3. Organic products

The surface treatment industry use a growing number of organic chemical products to enhance the quality of coatings (brighteners) or complexing agents such as, tertiary and quaternary amines, EDTA, etc., to promote deposition, especially in the case of co-deposits.

These chemicals have negative effects on the environment because they significantly increase the COD of the effluent and are difficult to eliminate.

IV.3. CURRENT TECHNIQUES FOR EFFLUENT TREATMENT

Most surface treatment workshops use physico-chemical techniques to purify liquid effluents. These consist of a combination of physical techniques, e.g. precipitation, decantation, filtration, etc., and chemical processes of oxidation-reduction to eliminate the contaminating metals in solution.

During the construction of plating workshops, several networks for the collection of waste-water streams are constructed to separate incompatible flows and to facilitate subsequent purification. Such networks would include pipework for:

- basic solutions and those containing cyanide,
- acidic and chromic solutions,
- acid/basic stream.

In this paper the treatment of these representative effluent streams will be considered.

In a physico-chemical purification scheme, three steps can be observed:

- initially the alkaline cyanide stream is oxidized in the alkaline environment to convert cyanides to cyanates; and the acidic chromic stream is reduced by bisulfite to transform Cr(VI) to Cr(III),
- then the above purified streams are mixed with the mixed acid/basic stream, and this mixture is treated with sulfuric acid or soda (lime is better) to adjust the pH to 6.5-9 to precipitate heavy metals as hydroxides,
- finally the precipitated hydroxides are decanted, filtered and dewatered in a press to separate water from hydroxide mud; the hydroxide mud is send to an agreed centre for treatment or disposal; and the water from decantation and the filter press, conforming to discharge limits, is send to sewage for disposal.

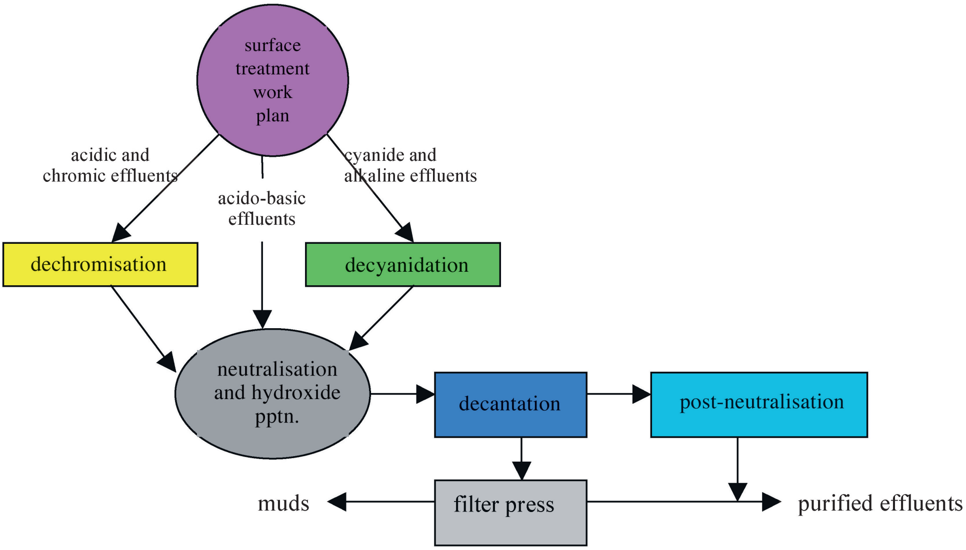


Figure 3.1. Scheme of a physico-chemical effluent treatment plant

IV.3.1. Different phases of purification in the above physico-chemical scheme

IV.3.1.1. First step – pre-treatment of effluents

Dechromisation

The chromic acid effluents (table 3.1) are treated in the dechromisation reactor with sodium bisulfite ($NaHSO_3$) and sulfuric acid (H_2SO_4) under mechanical agitation, to reduce Cr(VI) to Cr(III) by the following reactions:

$$H_2Cr_2O_7 + 3\ NaHSO_3 + 3\ H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\ NaHSO_4 + 4\ H_2O$$

or

$$4\ H_2CrO_4 + 6\ NaHSO_3 + 3\ H_2SO_4 \rightarrow 2\ Cr_2(SO_4)_3 + 3\ Na_2SO_4 + 10\ H_2O$$

Elements or polluting agents	Chromium/Acid effluent
pH	2.6
Total suspended solids	140 mg/L
Chromium(VI)	490 mg/L
Fluorides	5 mg/L
Chlorides	520 mg/L
Total cyanide	0.02 mg/L
COD (Chemical Oxygen Demand)	177 mg/L
Conductivity	7.2 mS/cm
Dry residue (105 °C)	4 930 mg/L
Total metals analysed	730 mg/L

Table 3.1. Typical composition of a chromium/acid effluent from a surface processing workshop before dechromisation

A value of the $pH \leq 2.5$ is required because the reduction kinetics for Cr(VI) to Cr(III) decreases quickly if the pH rises, the critical limit being pH 3.5 at which the reaction velocity becomes zero.

The reduction is continuously controlled by monitoring the pH and redox potential of the reaction.

This technique has been used for many years and gives very good results with residual $Cr(VI) < 0.1 mg/L$.

Advantages:

- easy supply and storage of chemicals,
- automatic control of mechanical operations, pumps, stirrers, etc.,
- automatic process control by measurement of pH and redox potential,
- proven efficiency,
- low operating cost.

Drawbacks:

- increase of effluent salinity due to added reagents,
- ventilation of storage area and reactors (evolution of toxic SO_2 from $NaHSO_3$ in acid),
- reagent consumption (Table below); in practice an excess of reagents is used as -part of them reduces any organic matter in the effluents.

	Quantity of reagent/g Cr(VI)	
Reagents	Theoretical	Practical
$NaHSO_3$ (mL) (40%)	5.7	7
H_2SO_4 (g) (conc)	0.95	1.2

Other dechromisation processes

Alternative reagents to sodium bisulfite to reduce Cr(VI) include SO_2, Na_2SO_3, $Na_2S_2O_4$, $Na_2S_2O_5$, and it can also be undertaken with the help of ferrous salts, as $FeSO_4$.

This practice of using iron (II) is not very common but it is interesting for workshops that practice sulfuric etching of steel on a big scale as, in this case, it is sufficient to mix the etching residues with the chromic acid effluent to reduce the Cr (VI) much more easily whatever the pH (between 1 and 8.5).

Drawbacks of this process are the formation of huge quantities of mud from iron hydroxide precipitation because $FeSO_4$ is added in large quantities for practical reasons (see table below); there is also a significant increase in the COD.

Reagent consumption:

	Quantity of reagent/g Cr(VI)	
Reagents	Theoretical	Practical
$FeSO_4, 7H_2O$ (g)	16	60-90
H_2SO_4 (conc.)	1.9	2.5

Implementation:

The Cr(VI) to Cr(III) reduction reaction requires a minimum reagent contact time of 20 minutes; this should be determined during the design of the dechromisation reactor and measurements should be calculated for a contact time of 30 minutes to ensure total reduction of the effluent.

The reduction reaction does not produce any toxic fumes provided that there is not an excess of bisulfite; if there is an excess, SO_2 fumes are produced. SO_2 will also be released at pH < 1.5, hence the need to regulate the pH.

Decyanidation

Table 3.2 gives the typical composition of a Cyanide/Alkaline effluent from a surface processing workshop before decyanidation.

The alkaline effluents containing cyanide are treated in the decyanidation reactor and under mechanical agitation with added bleach (sodium hypochlorite, NaOCl) and soda (NaOH) at pH >11.5 to prevent the emission of very toxic fumes of cyanogen chloride. The chemical oxidation of cyanides (CN^-) in cyanates (CNO^-) occurs in two steps:

$$CN^- + ClO^- + H_2O \rightarrow ClCN + 2\ OH^-$$
$$ClCN + 2\ OH^- \rightarrow Cl^- + CNO^- + H_2O$$

Overall the reaction is:

$$NaCN + NaClO \rightarrow NaCNO + NaCl$$

Elements or polluting agents	Cyanide/Alkaline effluent
pH	10.4
Total suspended solids	250 mg/L
Chromium(VI)	0 mg/L
Fluorides	3 mg/L
Chlorides	64 mg/L
Total cyanide	158 mg/L
COD	462 mg/L
Conductivity	10.9 mS/cm
Dry residue (105 °C)	4 420 mg/L
Total metals analysed	100 mg/L

Table 3.2. Typical composition of a cyanide/alkaline effluent from a surface processing workshop before decyanidation

The oxidation reaction is continuously controlled by measurement of pH and redox potential.

This technique has been used for many years and gives very good results with residual $CN^- < 0.1$mg/L.

Advantages:

- easy supply and storage of chemicals,
- automatic control of mechanical operations, pumps, stirrers, etc.,
- automatic process control by measurement of pH and redox potential,
- proven efficiency,
- low operating cost,
- low COD.

Drawbacks:

- increase of salinity of effluent due to the added reagents,
- ventilation of storage area and reactors,
- risk of emissions organo-chlorine compounds,
- not valid for cyanide concentrations > 2g/L,
- chlorine must be eliminated from the treated effluents,
- unstability of bleach solution,
- reagent consumption (see table below):

	Quantity of reagent/g Cr(VI)	
Reagents	Theoretical	Practical
NaClO (mL) (12.5% active Cl_2)	18.2	25
NaOH (g)	3.1	3.8-4

Other decyanidation processes

Persulfuric acid (H_2SO_5) can be used instead of bleach as oxidant, the advantage being the direct formation of cyanate CNO^- (without the intermediate step of cyanogen chloride) and, by hydrolysis, the transformation of cyanate CNO^- to carbon dioxide CO_2.

Reactions:

Direct transformation in cyanates CNO^-:

$$NaCN + H_2SO_5 \rightarrow NaCNO + H_2SO_4$$

Hydrolysis of cyanates:

$$NaCNO + 2\ H_2O \rightarrow CO_2 + NH_3 + NaOH$$

Other advantages are very good decyanidation, drawbacks are the possible formation of ammonium complexes and the need to maintain the pH above 9.5 to avoid the very toxic hydrocyanic acid fumes.

Consumption of reagents:

	Quantity of reagent/g CN^-	
Reagents	Theoretical	Practical
H_2SO_5 (mL) (conc.)	22	25 to 30
NaOH (g)	3.1	3.8 to 4

To destroy small amounts of cyanide it is also possible to use hydrogen peroxide (H_2O_2) as oxidant with copper as catalyst. This technique can be enhanced by the use of ultrasound, when the reaction is instantaneous.

Complex cyanides

Metals are easily complexed by cyanide and these complexes are very difficult to destroy, especially the complex cyanides of nickel and copper that can easily be formed by the mixing of effluents. It is therefore essential to ensure that there is no chance of the formation of cyanide complexes in the workshop effluents.

IV.3.1.2. Second Step - Neutralisation and precipitation

Neutralisation

The effluents following destruction of chromium (VI) and cyanides are mixed with the acid/basic effluents in a reactor controlled at pH between 6.5-9 by the addition of sulfuric acid or soda as appropriate. Such neutralisation has three goals:

- to obtain an effluent pH with no any danger to the environment,
- to precipitate heavy metals as insoluble hydroxides,
- to eliminate some anions such as phosphates, fluorides, and sulfates.

Ensuring insolubility of metal hydroxides

This is a difficult problem with effluents from surface processing especially in workshops that deposit many different metals. Indeed, according to the nature of metal and the pH value the extent of hydroxide solubility can vary considerably. Cadmium, for example, has a minimum solubility at pH 11, but if the effluents also contain chromium, zinc, or nickel, these can redissolve at this pH.

Therefore the pH value is of primary importance, and on its value is going to depend on the solubility of the metallic hydroxides and consequently the amount of heavy metals remaining in the effluent after treatment. The best solution, when effluents contain cadmium, is to treat this metal independently of the others by electrolysis, ion exchange, evaporation, etc.

Precipitation

The precipitation of the metallic hydroxides takes place during neutralisation. As the pH achieves the appropriate value for precipitation of the metal, some microflocs appear in the solution, and it is important to increase the size of these flocs to facilitate decantation. To increase floc size anionic organic flocculating agents are added to the effluents. The choice of such flocculating agents is undertaken from representative trials on the effluents.

IV.3.1.3. Third step – precipitate treatment

Decantation

After precipitation of the hydroxides, the effluents are generally decanted in a conical decanter, where feed enters at the centre of the cylinder and the removal of water takes place at the periphery toward the throat.

Pressing of the muds

Following decantation the hydroxide muds are pumped from the base of the decanter and fed to a filter press to separate the residual water. After dewatering the solid cakes of mud are transported to the agreed centres for treatment or disposal.

At the present time this physico-chemical decontamination system is used in more than 80% of the surface processing workshops in Europe.

The described process gives good results from the quality of the treated waters, but shows several drawbacks including:

- consumption of chemicals,
- consumption of water,
- high salinity of the decontaminated effluents,
- re-use of the water impossible without prior treatment due to the salinity,
- danger for environment in the case of system failure as there is no closed loop system,
- limitations in extent of decontamination.

IV.3.2. Other physicochemical processes for the purification of surface treatment effluents

In the design of a physicochemical purification flow-sheet two approaches are possible: reduce the toxicity of the incoming stream or treat the effluent from the process. The techniques described below consider both approaches.

IV.3.2.1. Electro-coagulation

This technique allows the co-precipitation of metallic hydroxides with aluminium, magnesium, or iron hydroxides generated in solution by anodic oxidation. The effluent to be purified is fed into an electrolytic cell the anode of which consists of aluminium, magnesium, or iron. When the current is on, Al^{3+}, Mg^{2+} or Fe^{2+} ions are produced at the anode and water is decomposed at the cathode with production of OH^- these ions combine to form the corresponding hydroxides:

$$Al^{3+} + 3\,OH^- \rightarrow Al(OH)_3$$
$$Mg^{2+} + 2\,OH^- \rightarrow Mg(OH)_2$$
$$Fe^{2} + 2\,OH^- \rightarrow Fe(OH)_2$$

These hydroxides promote the co-precipitation of other metallic salts in the effluent, and the addition of a flocculant and the emission of gases at the electrodes promotes the flocculation and flotation of the hydroxide precipitates (electro-flotation).

Applications

a) Purification of metal containing effluents

In the case of surface treatment effluents, the choice of anode (Al, Mg, or Fe) and the pH of the effluent depend on the nature of the pollutants in the effluents. The anodes may be rectangular sheets or cylindrical and the cathodes are stainless steel. Good results should be obtained by mixing two types of anodes (e.g. Al and Fe, or Mg and Fe). The pH must be maintained between 6-8 and the temperature of the effluent should not exceed 50°C.

An advantage of this process over classical hydroxide precipitation is the direct elimination of the precipitates by flotation. Some other pollutants, such as hydrocarbons and MES can also be removed.

b) Removal of inks and pigments from effluents

This process is very useful for the elimination of inks and pigments. These coagulate with the hydroxides, and the process of flotation permits direct elimination of the contaminants.

Advantages of the process:

- better elimination of metals and colloids,
- good solid-liquid separation.

Disadvantages:

- not suitable for cyanide effluents,
- consumption of metals (anodes),
- operating cost.

IV.3.2.2. Electrolysis

"Classical" electrolysis

"Classical" electrolysis by itself will not reach the required statuary discharge limits but can reduce the quantity of metals for treatment by the physicochemical processes. This technique is widely used to recover gold and silver from rinses and typically for metals such as cadmium and copper. To obtain good results, electrolysis must be carried out on a concentrated effluent with as large a cathode surface as possible.

Separated compartment electrolysis

There are three types of electrolysis with separated compartments:

- membrane electrolysis,
- electrolysis with ion exchange membranes (electro-electrodialysis),
- electrodialysis.

a) Membrane electrolysis

In this process the anode compartment is separated from the cathode compartment by a porous membrane. Migration of ions through the membrane is not selective but according to the nature of the membrane it is possible to electrolyse effluents that cannot be treated by "classical electrolysis.

Applications:

- selective electrolysis of effluents,
- recovery of metals where deposition in the traditional way is impossible because of toxic fumes or low output,
- regeneration of acid pickling baths.

b) Electro-electrodialysis

(see also Membrane processes in Section 3).[5]

Here an ion exchange membrane is used to separate the compartments. This technique is used to purify chrome baths from dissolved iron and to regenerate the bath. Some difficulties can occur during use from corrosion of the equipment and problems with the membranes.

At present, only chrome baths catalysed with sulfuric acid can be purified without large corrosion problems, fluorosilicate baths (high speed deposition chrome baths) are not suitable because the free fluoride causes intergranular corrosion.

N.B: in the course of the EU RECYCHROM project, new membranes have been developed that are more resistant and easier to clean.

Advantages:

- good purification of the bath,
- good bath regeneration.

Disadvantages:

- corrosion,
- membrane strength.

c) Electrodialysis

(see also Membrane processes in Section 3).[5]

Electrodialysis uses only the migration of species under the electrolytic field through the membranes and not the electrode redox mechanisms as in classic electrolysis or membrane electrolysis.

The electrodialysis cell is thus an "ion pump" and there is an ionic transfer between low concentration to high concentration effluent. That is why electrodialysis can be used to reconcentrate plating baths from rinse waters.

Applications:

- regeneration of silver and copper cyanide baths,
- regeneration of nickel baths.

Advantages:

- treatment of large volumes (> 10 m^3),
- good metal recovery,
- no toxic emissions.

Disadvantages:

- feasibility tests required,
- cost of the equipment and maintenance.

IV.3.2.3. Resin Ion Exchange

(See also Ion Exchange in Section 3).[4]

Ion exchange resins allow the retention of dissolved salts and the partial or in total clean up of diluted or concentred effluents. The ion exchange resins are available in the form of beads or powders, and are generally used in columns of capacity 50-100 L for mobile units, up to several hundred litres for fixed installations.

Several types of resins can be obtained:

- strong acid cation exchangers (sulfonic acid type) called “strong cation”,
- weak acid cation exchangers (carboxylic acid type) called “weak cation”,
- strong basic anion exchangers (quaternary ammonium) called “strong anion”,
- weak basic anion exchangers (secondary or tertiary amines) - “weak anion”,
- complexing or chelating resins.

a) Role of the resin

Strong acid cation exchangers:

- these exchangers retain all the cations over pH range 1-13,
- regeneration is performed with hydrochloric or sulfuric acids,
- relative cation affinities:

$Cr^{3+} > Al^{3+} > Pb^{2+} > Fe^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ag^{+}$

Weak acid cation exchangers:

- operate over a pH range 3-12,
- regeneration with hydrochloric or sulfuric acids,
- weak cation resins are not used with surface treatment effluents,
- relative cation affinities:

$Cu^{2+} > Pb^{2+} > Fe^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Ca^{2+} > Mg^{2+}$

Strong basic anion exchangers:

- retain anions over a pH range 1-12,
- particularly useful for cyanides species,
- regeneration with sodium hydroxide,
- relative anion affinities:

cyanide metal complexes >EDTA complexes>$NO_3^- > HCrO_4^- > Cl^- > CN^-$

Weak basic anion exchangers:

- retain anions at $pH < 5$,
- regeneration with sodium hydroxide,
- relative anion affinities:

cyanide metal complexes>$CrO_4^{2-} > SO_4^{2-} > NO_3^- > Cl^- > F^-$

Complexing or chelating resins:

- used for their selectivity for transition metal cations,
- relative cation affinities:

$VO^{2+} > Sr^{2+} > Ba^{2+}$

b) Exchange capacity

Because exchangers operate by an exchange of ions the exchange capacity is expressed in *equivalent weight per litre (eq/L),* where the equivalent is the molar mass of one ion divided by the charge on the ion:

Thus for silver, Ag = 108g and $Ag^+ = 1 \rightarrow 1$ eq $Ag^+ = 108/1 = 108$g of silver

and for copper, Cu = 64g and $Cu^{2+} = 2 \rightarrow 1$ eq $Cu^{2+} = 64/2 = 32$g of copper

- Useful resin exchange capacities for used in surface treatment industry:
  - strong cation: about 1 eq/L (resin),
  - strong anion: about 0.5 eq/L (resin),
  - weak anion: about 0.7 eq/L (resin).

c) Applications

Recycling of rinse water

- for acid and chromate rinse waters, the ionic exchange installation consists of:
  - one strong cation exchanger,
  - one weak anion exchanger,
  - and possibly one strong anion exchanger.

- for basic and cyanide rinse waters, the ionic exchange installation consists of:
  - one strong cation exchanger,
  - one weak anion exchanger,
  - one strong anion exchanger (obligatory if effluents contain cyanide).

Post-treatment after classical purification

After classical purification treatment, the effluent can contain heavy metals in concentrations between 0.1-10 ppm, which can be reduced to <0.1 ppm by resin ion exchange. Generally strong cation resins are used.

Deionised water production

The water to be deionised is successively treated with cationic, to remove cations, and anionic resins, to remove anions. The process of demineralisation is monitored by measurement of the conductivity of water, expressed in Siemens (S) or microSiemens (µS)

Exchangers	Water conductivity	Water pH
Strong cation + weak anion	50-5 µS	6-7
Strong cation + strong anion	20-1 µS	7-9
Strong cation + weak anion + strong anion	20-1 µS	7-9

The second and the third examples produce the same quality of water but if the feed water contains large quantities of sulfate and chloride, the third example is economically preferable.

For ultra-pure deionised water, the use of mixed beds of anion and cation resins produces water with conductivities from 0.05-1 µS.

d) Advantages and disadvantages of ion exchange resins

Mobile resins columns (generally for rinse water treatment)

This type of resin installation is widely used in small workshops with low pollutant fluxes.

Advantages:

- good quality of water purification,
- easy control and maintenance,
- possibility of external regeneration of resin.

Disadvantages:

- high sensitivity to oil and organic compounds (fouling),
- saturation of the cationic exchanger before the anionic resin (precipitation of heavy metals and blocking of column),
- capital and operating costs.

Fixed resins beds (generally for deionised water production and purification of rinse waters)

These types of installation allows the production of deionised water in small or large quantities, column regeneration is very simple and no treatment of the regeneration effluents is required (if the pH is from 6-9).

For purification of rinse waters containing heavy metals, the regeneration effluents contain the removed heavy metals and must be purified in the waste-water plant of the workshop.

Advantages:

- excellent output of deionised water from feed water containing calcium and magnesium salts (hard water),
- easy control and maintenance,
- internal regeneration simple,
- no specific treatment of the regeneration effluents (deionised water production).

Disadvantages:

- possibility of precipitation of calcium sulfate in column if regenerated with sulfuric acid,
- treatment of the regeneration effluents (from purification of rinse waters).

IV.3.2.4. Liquid-liquid (solvent) extraction

Liquid-liquid extraction is a process in which one or several constituents of an aqueous phase are transferred into an organic phase (or the inverse), the two liquids being immiscible.

In the first step the two liquid phases are mixed, in this step there is a transfer of the solute (C) from the aqueous phase (S1) to the organic phase (S2). The second step is separation of the mixed phase into the two phases but now the organic phase (S2) contains more solute (C) and the aqueous phase (S1) less solute (C). Further extractions are performed until the solute is eliminated from the aqueous phase. To recover metals organic extractants (liquid ion exchangers) that are soluble in the organic phase can be used to selectively complex with individual metals. These liquid ion exchangers as the name implies, are similar in functionality to the ion exchange resins, i.e. carboxylic acids, amine bases, and chelating acids.

a) Advantages

- selectivity of the exchangers for metals,
- extraction/stripping operations easy to perform,
- simple control and monitoring of process,
- recyclability of extractants,
- low operating costs.

b) Disadvantages

- fire risk from use of organic solvents and VOC emissions,
- entrainment of phases giving poor effluent quality,
- emulsification of phases with poor separation.

c) Extraction devices

Two kinds of extraction device are on the market, mixer-settlers and column extractors:

Mixer-settlers consist of a mechanically agitated mixer where the two phases are mixed joined to a settling tank where the mixed phase separates into the two immiscible phases under gravity. These units are most effective when they are joined together to give a number of stages of mixing/separation.

Advantages:

- effectiveness of each stage and ability to add more stages easily,
- easy monitoring,
- effectiveness whatever the viscosity.

Disadvantages:

- investment cost,
- emulsification of the two phases and entrainment of phases.

Column extractors unlike mixer-settlers are not divided into stages but consist of a column fitted with various types of mechanical or pulse agitator to mix the two phases. The heavy (aqueous) phase enters at the top of the column and flows counter-currently to the light (organic) phase. During passage through the column droplets of the two phases continuously mix and separate and transfer the solute between them.

Advantages:

- effectiveness,
- ease of operation.

Disadvantages:

- difficult monitoring of the columns,
- losses from entrainment and drag-out,
- maintenance.

d) Applications

Liquid-liquid extraction has been proposed for the treatment of a range of different effluent streams including rinse waters, spent etching, pickling and plating baths, allowing purification and recovery of valuable materials.

Thus it has been used for the regeneration of acid bath, mainly for recovery of phosphoric acid which is expensive. In the surface treatment industry, phosphoric acid is widely used in the chemical brightening of aluminium before anodisation and for large workshops that use several hundred tons of phosphoric acid, liquid-liquid extraction is a good alternative technique to classical lime precipitation especially as 95% of the acid can be recuperated from a uses bath almost without production of any muds. This process becomes economic for plants using more than 500 t/y phosphoric acid.

In the setting of the IPPC Directive, surface processing workshops are required to use the best techniques currently available and to protect the environment by using such techniques in a closed circuit.

IV.4. TECHNIQUES FOR TOMORROW: BEST AVAILABLE TECHNIQUES TO LIMIT POLLUTION FLOWS (BAT)

Numerous technologies designed to limit polluting flows are currently available. Many comprise flow reduction techniques used upstream and/or downstream of decontamination plants. If they are not sufficient in themselves to meet the discharge limits fixed in the regulations, they reduce the pollution flows discharged into the natural environment and sometimes lead to a zero liquid discharge on-site.

Each technique only applies to certain pollutants in a given operating environment, which explains why several techniques can be complementary or combined in a particular application. Because of this it is important to define the characteristic effluents of surface treatment operations and to study the most appropriate technologies for the industry. Naturally, the technical and economic considerations specific to the production concerned such as volumes, production rates, treatment line capacities, etc., must not be ignored. In particular, it is essentially important to ensure that the solution chosen will not have any negative effects on the production rate or the quality of the treated work pieces.

The existing technologies considered to be pertinent to the characteristic effluents from surface treatment processes are described below. Of those technologies available today which enable zero liquid discharge on-site to be achieved, as well as being suitable to treat the specific features of surface treatment effluents, the best include the following:

- evaporation technologies,
- membrane technologies.

Depending on the nature of the effluents and the water reuse requirements dictated by the production processes, membrane techniques can be used both upstream and/or downstream of evaporation:

- to limit the water consumption,
- to limit the consumptions of chemicals,
- to “pollute less to clean up better”.

Under these conditions, the use of clean technologies, evaporation and membranes, allows the decontamination of the workshop effluents and the recycle of water at an acceptable cost.

IV.4.1. Control of pollution streams and implementation of Best Available Techniques

A thorough knowledge and control of the production process are an effective way of respecting the principle of "Pollute less to clean up better". In a conventional production activity, the quality of the final product depends on a certain number of parameters previously identified and controlled. The control of pollution from surface treatment processes depends on the following:

- the production process used, with the limits due to the chemical and electrochemical reactions imposed by the deposition conditions,
- the type of process operation, i.e. discontinuous "batch" or continuous operation, addition of reagents, etc.,
- the process environment: temperature, flow rates, energy, etc.,
- the personnel involved: experience of operators, training, etc.,
- the raw materials used: e.g. nature and quality of reagents,
- the control equipment: diversity of measuring and analysis equipment and instrumentation.

A surface treatment sequence consists of a series of operations that can be represented diagrammatically by a set of "modules" each consisting of a specific activity with precise functions, e.g. degreasing, stripping, coating, etc. Each activity module generally consists of an active part which carries out the treatment (bath) and a rinsing function. Each module is thus a source of polluting emissions with different mass flow rates.

The identification and characterisation of the above streams, as close as possible to their source, will enable their impact on the purification processes used (BAT) to be controlled. Corrective actions to control the flows, specific to each basic stream, are not necessarily of a material order. They can sometimes concern the actual organisation of the different surface treatment operations. This type of corrective action, which is not equipment-orientated, is based on the concept of "best practice" and can lead to substantial investments whose level of profitability very often proves to be short-term.

Their aim, in particular, is to reduce:

- drag-in, drag-out volumes,
- water consumption,
- variability of the active product and pollutant concentrations.

Their application in a surface treatment unit can also:

- limit the amount of chemicals used,
- improve the production process (quality, cost) as well as the hygiene and safety of personnel.

The “good practice” that can be used in a surface treatment unit include the following:

- *implementation of the polluted effluent control* which consists of identifying the various factors that affect the process, and more especially:
  - identifying exceptional causes that have an impact on the process, by going as far upstream possible of the problem posed by the pollution concerned,
  - monitoring, by means of analysis, the representative parameters of polluting streams, e.g. metals, hydrocarbons, COD, suspended solids, etc.

- *inspection and regular monitoring of baths* by means of scheduled analyses leading to appropriate adjustments results in:
  - increasing bath life,
  - improving the quality of the final work pieces treated.

  As a result, it is possible to work with baths that remain effective for longer periods of time.

- *elimination of systematic bath-emptying programmes*

  When the composition is regularly monitored, it is no longer necessary to systematically empty treatment baths according to a predetermined frequency. Thus replacement is only required if the content of undesirable substances reaches an unacceptable level in relation to the required production quality.

  Whatever the circumstances, it is always better to use treatment baths for a quantified maximum time based on feedback, production quality, disposal and replacement costs, volume of flows, etc. Emptying is only carried out after analysis and comparison with the quantified maximum time.

- *external treatment as an alternative to physico-chemical treatment of certain concentrated baths*

  Certain concentrated baths, when treated internally even at extremely small quantities of solution, are often the source of highly polluting streams that are detrimental to correct operation of the decontamination system. Thus outsourcing or “treatment by an external centre” should be considered.

  It should be noted that in the case of internal treatment using evaporation, certain baths have higher concentrations than can be concentrated by an evaporator. It is therefore unwise to treat baths with a “dry residue” content of more than 200 g/L since the concentration factor will only be in the order of 2.

- *implementation of written procedures*

  The implementation of written and evaluated procedures eliminates many of the deviations that affect the production process and encourages the use of technologies that reduce polluting emissions.

- *handling of chemicals by specialised personnel*

  The preparation of baths, addition of reagents and other manipulations using chemicals are subject to strict regulations. It is important for such activities to be carried out by specialised personnel trained for this purpose, not only for quality and economic reasons, but also in the interest of hygiene and safety.

- *strict control of chemical stocks*

  Management of stocks of chemicals must not be neglected. Poor management can affect process control and reagent consumption.

- *implementation of multi-stage dynamic rinsing (counter-flow cascade)*

  This type of rinsing operation, instead of conventional single-stage rinsing, considerably reduces the amount of water required, while producing the same quality of washing. In addition smaller equipment can be which is therefore less expensive.

- *implementation of water spray rinsing*

  Spray rinsing can be likened to multi-stage dynamic rinsing. Compared with static or single-stage dynamic rinsing, better rinsing quality can be achieved in certain cases using this type of washing.

- *reuse of rinse water*

  It is often more economical to top up hot treatment baths with water from previous rinses to compensate for evaporation. This operation can be carried out using either static or cascade rinse water at a flow rate appropriate to the evaporation loss.

  As in any case of water reuse, its fitness for the intended use must be carefully examined, and that no chemicals remain in the water which could alter the composition of treatment bath as a result.

- *optimisation of extraction and drip times*

  Since pollution flows depend on the drip time of the work piece, it is useful to optimise the time during which the work pieces remain outside the tank.

- *minimisation of solution retention volumes or drag-in/drag-out volumes*

  Since the pollution flow depends on the drag-in/drag-out volumes, any action to reduce them is importance, particularly when sizing pollution treatment equipment (BAT). For example, different positioning of work pieces and supports, an extra quarter-turn of the barrel or the use of a forced drag-out system are all effective ways of reducing the drag-in/drag-out volume.

- *control and continuous monitoring of rinsing quality parameters*

  Regular monitoring of rinsing, like that of treatment baths, results in: better quality, due to consistently efficient rinsing, provided that quality level is kept between two predefined values or in the vicinity of a specific set-point; lower water consumption, because only water that does not meet the rinsing quality control standard is treated.

- *implementation of flow limiters or other systems designed to save water (e.g. timers)*

  For a given rinsing quality, it is not usually necessary to maintain a constant water supply. It is more economical to adjust the water supply according to the rinsing activity (surface area treated, number of barrels, etc.).

IV.4.2. Evaporation techniques

(see also Evaporation in Section 3).[3]

Evaporation is a concentration technique having numerous advantages, including the capacity to separate a concentrated stream containing the solid matter from a distillate composed of pure water for reuse.

An evaporator consists of a boiling chamber or boiler connected to a cooling system or condenser. The effluent is heated in the boiler causing the water to evaporate. This water vapour then condenses when it comes into contact with the cooling system forming a condensate (or distillate). Evaporation of water inside the boiler causes an increase in the concentration of compounds that increases the boiling temperature of the solution above that of water resulting in the formation of a concentrate.

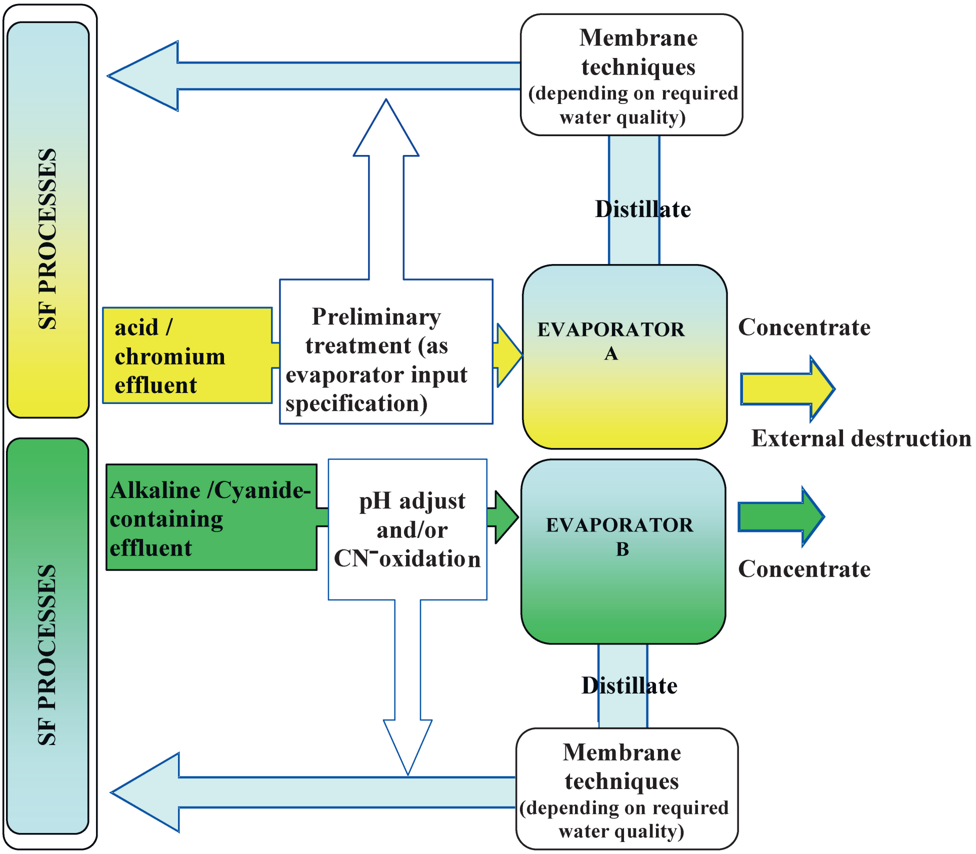


Figure 4.1. Operating flow-sheet for treating effluents from surface finishing processes incorporating BAT

Volatile substances whose boiling points are lower than water and thus have higher vapour pressures than water will co-distil and condense with water in the condensates and prevent the condensed water from being reused. If the volatility is high, the concentration of the most volatile product in the vapour generated initially can be very high, but it will rapidly diminish during further evaporation.

This can be a problem with the evaporation of effluents containing free cyanide as hydrocyanic acid is volatile and can appear in the condensate. The amount of cyanide in the condensate will depend on the pH of the effluent entering the evaporator (see Tables 4.1, 4.2). Also evaporation of acidic effluents containing fluorides or chlorides can lead to the condensate being contaminated with these ions. Similarly in the case of alkaline effluents, the presence of ammonium-containing substances will contaminate the condensate with ammonia.

The data below shows that when the pH < 9.3 (pK_a of the HCN/CN^- reaction), the predominant species in the HCN/CN^- equilibrium is HCN. Thus using an effluent pH >10 is recommended.

Concentration of free CN^- in typical cyanide effluent (mg/L)	pH of effluent	Concentrations of different cyanide species in the effluent (mg/L)	
		HCN	CN^-
100	8.3	90.9	9.1
	9.3	50	50
	10.3	9.1	90.9
	11.3	1	99
10	8.3	9.1	0.9
	9.3	5	5
	10.3	0.9	9.1
	11.3	0.1	9.9

Table 4.1. Predominating species in a cyanide-containing effluent according to pH

Using the liquid/water vapour equilibrium constants for the HCN/H_2O system, the data below shows the CN^- concentration in the liquid phase (condensate), as a function of the mass of HCN present in 1 kg of water vapour. Thus when evaporating a cyanide-containing effluent, the higher the concentration of HCN the more the distillate will be polluted with cyanide.

Mass of HCN (mg) in 1 kg of water vapour at 35 °C (1)	Concentration of CN^- in the liquid phase (mg/L)
100	4
10	0.4
1	0.04

(1) coefficient of relative volatility of HCN in water $\alpha = 25$

Table 4.2. Cyanide concentration in equilibrium (liquid/vapour phases)

Potential applications for evaporation in the field of surface treatment include:

- the production of water for rinsing operations (recycling of distillates),
- the concentration of rinsing effluents for re-introduction into the preceding treatment bath (recycling of concentrate),
- the purification of treatment baths to maintain their nominal concentration.

The following types of equipment can be used:

- a heat pump type evaporator,
- an evaporator using mechanical vapour compression,
- a multiple-effect evaporator,
- an atmospheric evaporator.

The choice of equipment will depend on the characteristics of the installation, e.g. flow rate, amount of effluent, delays in reaching boiling point due to the products present, etc. Further details of the equipment and related flow diagrams can be found in Section 3 of this publication.

The use of a reduced-pressure evaporation heat pump system provides a number of advantages for SMEs because of their ease of implementation and small dimensions. Also the use of reduced-pressure evaporation decreases the temperature of evaporation with the resulting advantage of limiting any degradation of the bath components so that the concentrate can be recycled.

Atmospheric evaporation, which requires a lower capital outlay, has the following main drawbacks: high energy cost in relation to the amount of water evaporated, and emission of pollution into the atmosphere, unless additional steps are introduced to treat the emitted vapours.

Increase in the concentration of the different substances present inside the boiling chamber can lead to the formation of highly corrosive gases. This can lead to corrosion of the heating elements in the evaporator, particularly when volatile acids such as hydrochloric acid and hydrofluoric acid are present. Note that increasing the concentration by a factor of 10 reduces the pH by one point.

IV.4.3. Membrane processes

(see also Membrane Processes in Section 3).[5]

Membrane processes operate below micrometer scale, that is, they enable separations to be made on a molecular level. The figure below shows that, for ion retention, two techniques are available: reverse osmosis and nano-filtration.

The selection criteria depend on the characteristics of the substances to be separated (molecules, ions), those of the membrane (dimensions, geometry, chemical nature, physical state, electrical charge, etc.) and the hydrodynamic operating conditions. Depending on these characteristics, the selective transfer of substances depends on the following:

- their size with respect to that of the membrane pores,
- their ability to diffuse through the membrane material,
- their ionic exclusion,
- absorption phenomena which may occur on the membrane as well as chemical reactions between the substances in solution and the membrane,
- combination of various parameters.

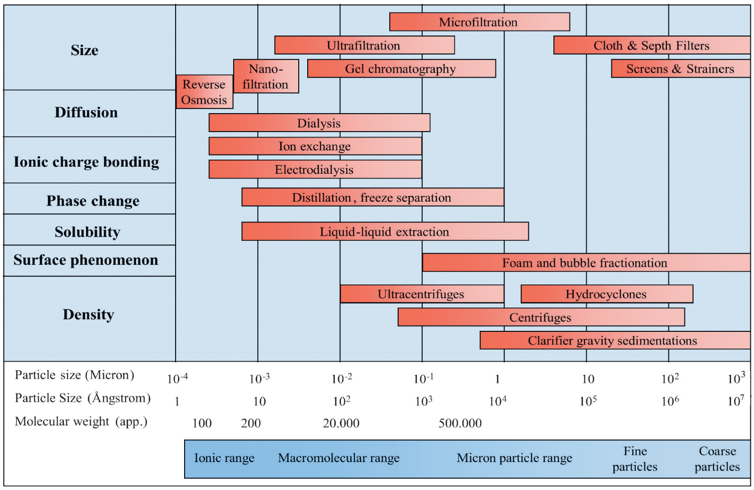


Figure 4.2. Technologies for the separation of species depending on their physico-chemical characteristics.

The process of membrane separation can be achieved in a number of ways depending on the physico-chemical characteristics of the species involved, for example: size, solubility/ diffusion, and charge. This leads to the different technologies of: filtration (size), reverse osmosis/dialysis (diffusion) and electrodialysis (charge). As noted above (Figure 4.2) nanofiltration (NF) and reverse osmosis (RO) are suitable technologies to treat surface treatment effluents as:

- their fairly high capacity to retain ions and molecules are similar to those present in the effluents,
- treatment rates are appropriate.

These two technologies are distinguished by the type of membrane used and the operating parameters. In the case of nano-filtration the membrane consists of a porous organic or mineral material with a pore size of 1-5 nm. On the other hand membranes for reverse osmosis are organic polymers with a dense structure.

Both processes rely on a pressure difference across the membrane to achieve separation of water that passes through the membrane (permeate) from the dissolved solutes (retentate). These technologies are mainly differentiated by their rejection rate, i.e. the capacity to limit the amount of dissolved salts, which in case of nano-filtration is 85% and lower than for reverse osmosis (93-99%).

In the case of reverse osmosis because the membrane has a small pore size the pressure difference is much higher and must exceed the characteristic osmotic pressure of the effluent. The choice of operating pressure is based on technical and economic criteria. However, it is limited by the mechanical strength of the membrane and the cost of the equipment required.

The flow rate of the solvent through the membrane depends on the operating pressure. It also depends on the permeability of the membrane to the solvent (water).

One of the main disadvantages encountered both in nano-filtration and reverse osmosis is clogging of the membranes by suspended solids and organic deposits. Depending on the tendency for clogging of the effluent, preliminary treatment may be required upstream of the NF or RO equipment (media filtration through sand, diatoms, etc., micro-filtration, and ultra-filtration). Preliminary treatment obviously affects the investment outlay and operating costs.

IV.4.3.1. Nanofiltration (NF)

The selectivity of NF membranes is influenced by the charge on to the membrane by the solution, particularly in the case of mineral membranes, and the valence of the ions in the effluent. The following points can be noted in this respect:

- the specific retention (ability to separate a particular substance) is influenced to a large extent by the pH of the solution, which can affect membrane polarisation,
- variation in the composition of the effluent can result in considerable variation in the composition and quality of the permeates,
- monovalent ions can pass through the membrane,
- molecules of identical size but with different charges can be separated.

Typical processing parameters for NF include an operating pressure across the membrane between 0.7-4 MPa and higher flow rates, up to 200 L/hr/m^2 membrane, can be achieved than for reverse osmosis.

IV.4.3.2. Reverse osmosis (RO)

As noted above RO membranes have a high retention capacity. However as the membranes become porous in highly alkaline ($pH > 12$) and highly acidic environments ($pH < 2$), their operating pH range is between 2 and 11. Outside this operating range, permeates of mediocre quality are obtained. Thus for industrial effluents such as those encountered in surface treatments, preliminary treatment to adjust the pH is necessary. An optimum operating pH must be determined to prevent precipitation in the solution or in proximity to the membrane, due to the secondary polarisation phenomena that can occur when the operating pressure is high.

The processing parameters for RO are typically an operating pressure range between 1.2-10.5 MPa. The flow rates obtainable depend on the osmotic pressure of the effluent, thus in the case of effluents with a low osmotic pressure (i.e. low concentration), flow rates in the order of 40-60 $L/hr/m^2$ membrane surface are possible.

In the presence of high concentrations of certain substances in the effluents, and depending on the concentration factor required, a “multi-stage” installation is often necessary.

IV.4.4. Definition of characteristic effluents from surface treatment activities

The concept of including evaporators and membranes to achieve zero liquid discharge on-site is based on a knowledge of the effluents generated by surface treatment activity. The chemical compositions most representative of the management methods, emptying of baths, internal treatment, continuous treatment, etc., and coating treatments used for the work pieces were sought.

Effluent treatment plants are required to manage various types of liquid wastes, particularly used baths (concentrated effluents), static rinses (semi-concentrated effluents) and dynamic rinses (diluted effluents). To manage these streams while taking into account the compatibility of the different chemicals, two categories of effluents can be defined for any surface treatment activity:

- a “chromium/acid” group including all the acid and chromium effluents,
- a “cyanide/alkaline” group with all alkaline and cyanide-containing effluents.

The average composition of each stream (Table 4.3) was obtained by analysing representative effluents of the multi-treatment industrial activities of European SMEs (employing 20-200 people) during the European project Tozeliwa (Towards Zero Liquid Wastes). The following treatments were considered:

- decorative or technical nickel/chromium and chromium (hard chrom) electro-plating,
- zinc and cadmium electroplating,
- chemical coatings such as nickel,
- anodic oxidation of aluminium.

Pollutants	"Chromium/Acid" effluent	"Cyanide/Alkaline" effluent
pH	2.6	10.4
Total suspended solids	140 (mg/L)	250 (mg/L)
Chromium(VI)	490 (mg/L)	0 (mg/L)
Fluorides	5 (mg/L)	3 (mg/L)
Chlorides	520 (mg/L)	64 (mg/L)
Total cyanide	0.02 (mg/L)	158 (mg/L)
COD (Chemical Oxygen Demand)	177 (mg/L)	462 (mg/L)
Conductivity	7.2 (mS/cm)	10.9 (mS/cm)
Dry residue (105 °C)	4 930 (mg/L)	4 420 (mg/L)
Total metals analysed	730 (mg/L)	100 (mg/L)

Table 4.3. Composition of characteristic surface treatment effluents (Tozeliwa project)

It is obvious that in the case of activities in which single treatments are more prevalent, the average composition of each category will differ. However the variations observed in parameters such as the pH, dry residue, and total amount of cyanide-containing and chromium(VI)-containing effluents had no significant effect preventing implementation of the concept.

IV.4.4.1. Implementation of vacuum evaporation

It was shown above that the presence of cyanides in a liquid effluent leads to fairly high pollution of the distillate. The cyanides must therefore be treated before evaporation by adjustment of the pH ($pH > 9.3$) which, although it does not alter the cyanide concentration of the effluent, it influences the quantity of cyanides transferred to the distillate (Tables 4.1, 4.2), or oxidation.

a) Treatment of cyanides before evaporation

As noted above cyanides can be oxidised by several reagents. However the use of salts such as sodium hypochlorite in alkaline solution increases the level of salinity in the effluent that in turn limits the volume concentration factor (VCF) that can be obtained by using either membrane or evaporation processes. As a result, another reagent hydrogen peroxide was chosen, which has the advantage of not increasing the salinity level of the effluent. A bibliographic study demonstrated the advantage of using the hydrogen peroxide to destroy cyanides. However as the hydrogen peroxide reaction is extremely slow, a catalyst usually copper is used that can be activated by, among others, UV radiation or ultrasound. It was found that this procedure requires good control of a number of parameters. Good results were obtained with the system activated by low frequency ultrasound (20-36 kHz) and adjustment of the amount of peroxide added according to the oxidation reduction potential of the solution. Other parameters that were important:

hydrogen peroxide/cyanide mole ratio of 5-6,
contact time in the reactor, 15-45 minutes,
amount of copper metal catalyst, 15-30% of CN^- content of effluent.

Under these conditions more than 99% of the cyanide in a characteristic cyanide-containing effluent was destroyed.

b) Corrosion tests on evaporator materials

Since evaporation increases the concentration of effluents in the boiling chamber, the materials used to construct the evaporator must be inert with respect to the effluents, especially as a volume concentration factor (VCF) of 5 to 20 can be obtained. Under such conditions, the environment created inside the evaporator by the release of corrosive gases, and/or the presence of corrosive substances in the effluent, can be aggressive even with respect to stainless steel. Corrosion phenomena e.g. pitting, deposit corrosion, differential aeration, can occur particularly in the presence of high concentrations of the above corrosive substances or precipitates.

To help selection of the most suitable evaporator materials appropriate to the composition of the effluent to be treated, corrosion tests were carried out on various alloys used by material suppliers, including stainless steels and nickel-chromium-molybdenum alloys (Table 4.4). Corrosion tests were conducted during the Tozeliwa project using the two conventional techniques: monitoring the free potential as a function of time, and monitoring the current density as a function of voltage, at a temperature of 35°C, corresponding to the operating temperature of the vacuum evaporators.

Alloys	Acid effluent			Alkaline effluent	
	with Cl^-, F^- and oxidant	with Cl^-, F^- <100 mg/L, pH <3	after adjustment pH > 4.5-5	with Cl^- > 200 mg/L	after adjustment pH >9.3
STEELS					
AISI 316L (X2CrNiMo 18-10)	No	No	No	No	Suitable
S 32750® (X2CrNiMoN 25-7-4)	No	Suitable	Suitable	Suitable	Not necessary
S 32760® (X2CrNiMoCuWN 25-7-4)	No	Suitable	Suitable	Suitable	Not necessary

Alloys	Acid effluent			Alkaline effluent	
	with Cl^-, F^- and oxidant	with Cl^-, F^- <100 mg/L, pH <3	after adjustment pH > 4.5-5	with Cl^- > 200 mg/L	after adjustment pH >9.3
Ni-Cr-Mo ALLOYS					
Hastelloy® C-22®	Suitable	Not necessary	Not necessary	Not necessary	Not necessary
Hastelloy® C-2000®	Suitable	Not necessary	Not necessary	Not necessary	Not necessary

Table 4.4. Choice of suitable evaporator materials for surface treatment effluents
During corrosion tests, particular attention was paid to the steel/weld interfaces and the welds themselves, as these are most sensitive to corrosion and therefore need to be very carefully monitored

Based on the corrosion tests and according to the experience of the material suppliers, it can be seen that the choice of materials is related to the type of effluents. The presence in the effluents of aggressive substances such as chlorides and fluorides, and oxidants e.g. chromium(VI), together with the acidity of the medium, must be taken into account when choosing construction materials for evaporators.

In the case of chromium acid effluents, adjustment of the pH to 4.5-5, before evaporation can enable a lower grade and therefore less costly material to be used. For cyanide-containing alkaline effluents, less corrosion is observed. The major problem concerns the pollution of distillates by cyanides.

c) Quality of the effluents obtained after evaporation

Following evaporation the distillates obtained (Table 4.5) are of a sufficient quality to be reused in the surface treatment process.

Parameters	Effluent entering the evaporator (mg/L)	Distillate without pH adjustment of incoming effluent (mg/L)	Distillate after adjusting incoming effluent to pH = 5 (mg/L)
pH	2.7	4.5	3.9
Ag	< 1	< 0.10	< 0.10
Al	27.8	< 0.10	< 0.10
Au	1.7	0.10	< 0.05
Cd	< 0.5	< 0.05	< 0.05
Cr total	560	< 0.10	< 0.10

Parameters	Effluent entering the evaporator (mg/L)	Distillate without pH adjustment of incoming effluent (mg/L)	Distillate after adjusting incoming effluent to pH = 5 (mg/L)
Cr(VI)	400	< 0.02	< 0.02
Cu	25.6	< 0.05	< 0.05
Fe	4.5	< 0.10	< 0.10
Ni	11.3	< 0.10	< 0.10
Pb	2.0	< 0.10	< 0.10
Sn	2.0	< 0.20	< 0.10
Zn	19.5	< 0.05	< 0.05
Ca	201	0.16	0.09
K	160	< 0.10	< 0.10
Na	2 450	< 0.10	< 0.10
Fluorides	2.0	< 0.5	< 0.5
Phosphates	< 10	< 0.15	< 0.15
Sulfates	211	< 1.0	< 1.0
Chlorides	600	< 1.0	< 1.0
Total cyanides	< 0.03	< 0.03	< 0.03
Total phosphorus	7.7	< 0.05	< 0.05
COD	172	80	105
Conductivity	22 400 $\mu S.cm^{-1}$	11.8 $\mu S.cm^{-1}$	24.5 $\mu S.cm^{-1}$

Table 4.5. Results of tests using vacuum evaporation on chromic acid effluents

IV.4.4.2. Implementation of membrane processes

Membrane techniques (nano-filtration and reverse osmosis) can be applied to:

- diluted effluent generated by the evaporator (distillate),
- effluents directly generated by surface treatment, i.e. chromic/acid or alkaline/cyanide streams.

The application of membranes to diluted effluents is well established and allow an acceptable quality of permeates for reuse. Volume concentration factors (VCF) of 15 were confirmed in the Tozeliwa project.

The application of membranes on concentrated effluent is not so obvious. The purpose which could motivate the treatment of the concentrated effluents by membranes processes is the possibility of reducing the polluted stream to be treated by the evaporator. In this way, the evaporator would have to treat a reduced volume of membrane retentates generated during pre-treatment. This would allow a smaller size evaporator to be designed providing the permeate obtained from the membrane process had an acceptable quality.

Laboratory tests on acid/chromic and alkaline/cyanide-containing effluents showed better retention for alkaline/cyanide-containing effluents.

The membranes used were:

- for nano-filtration (NF): an organic membrane (polyamide film), PCI AFC-30,
- for reverse osmosis (RO): an organic membrane (polyamide film), PCI AFC-99.

Quality of the effluents obtained after treatment by NF and RO

Using NF as a single technique does not generally allow a permeate to be obtained with satisfactory quality because of the difference in selectivity of monovalent, divalent, and trivalent ions. This selectivity depends on the charge taken by the membrane during operation.

In particular, in the case of chromium(VI)-containing effluents with higher concentrations than the characteristic acid-chromic effluent, the tests using NF show this technique is not suitable when used alone as a single technique (Table 4.6).

The use of RO as a single technique leads to a much better quality of the permeate than with the single NF, but the quality is still insufficient to permit reuse of the permeates without additional treatment (Table 4.6). The major disadvantages are the low specific flow rates (L/h/m²) and volume concentration factors (VCF), requiring a design with increased membrane surface and higher working pressure.

Parameters	Nanofiltration (single process)		Reverse osmosis (single process)	
	Effluent entering (mg/L)	Permeate (mg/L) VCF=9	Effluent entering (mg/L)	Permeate ($mg.L^{-1}$) VCF=3
Cu	49	1.7	14	0.2
Fe	201	1.8	45	0.5
Co	0.4	0.1	0.2	< 0.2
Na	1 012	352	638	14.6

Parameters	Nanofiltration (single process)		Reverse osmosis (single process)	
	Effluent entering (mg/L)	Permeate (mg/L) VCF=9	Effluent entering (mg/L)	Permeate (mg.L^{-1}) VCF=3
Cr(VI)	1 790	865	1 132	68
Cr(III)	155	98	56	2
Pb	1.1	0.5	1.2	0.3
Ni	43	0.7	15	0.3
Al	15	0.5	4.1	< 0.2
Mo	6.0	0.9	2.8	< 0.2
Zn	3.3	0.2	1.6	0.05
SO_4^{2-}	2 960	200	1 480	45

Table 4.6. Effluent quality following single application of NF or RO

Considering the use of single membrane processes was not technical feasibility for characteristic surface treatment effluents, the possibility of combining NF and RO techniques together with pH adjustment was considered. The results are given in Table 4.7.

The quality of the resultant permeate is acceptable. The fact that the specific flow rates are low will require equipment with appropriate increase in membrane area. The economic consequence of the use of membranes techniques upstream to the evaporator to reduce its size requires case by case study to optimise the possibilities.

Parameters		Effluent entering	Permeate FCV=2
pH		2-3	6
Cr(VI)	mg/L	1 700	not determined
Cr total	mg/L	1 900	< 1
Pb	mg/L	0.43	< 0.1
Ni	mg/L	62.3	< 0.05
Al	mg/L	11.5	< 0.2
Cu	mg/L	69.7	< 0.06
Fe	mg/L	210	< 0.05
Zn	mg/L	80	< 0.02
Na	mg/L	1 160	< 50
SO_4^{2-}	mg/L	6 600	< 10
Conductivity	µS/cm	21 900	13

Table 4.7. Effluent quality following combination of NF and RO with pH adjustment

IV.4.4.3. Implementation of the technologies

Based on the results obtained for each of the above technologies taken individually the implementation of them to illustrate the principle “pollute less to clean better” can be divided into five phases:

1) characterisation of acid/chromium and alkaline/cyanide-containing effluents (composition and flow rates),
2) implementation of “good practices” to reduce flows,
3) implementation of one or several appropriate evaporators,
4) choice of preliminary treatments before evaporation e.g. pH adjustment and/or oxidation/reduction reactions, multi-stage filtration,
5) definition of water quality required for total distillates reuse in the production unit which will determine whether or not post-treatment will be necessary.

These different phases involve investment and operating costs which will need to be defined so that the economic feasibility of the configuration resulting in “zero liquid discharge on-site” can be determined. The following section presents the economic data required for this analysis.

a) Cost evaluation

This section summarises the answers to a series of questions posed to the equipment suppliers. The aim of the information below is to present, as simply as possible, the operating and investment costs involved to treat the characteristic surface treatment effluents generated in SMEs. The effluents flow rates considered vary from 200-5000 m^3 per year *after the implementation of “good practice”*. This range covers the flow rates generally encountered in SMEs when rinses and dumping volumes are considered.

The economics of the overall process depend on a number of specific factors including: the country where the SME is based (different labour and energy costs, etc.) equipment suppliers, and whether or not certain ancillary items which are not always identified in the commercial offer (storage tanks, pumps, probes, etc.) are included in the main equipment. Because of such variations the economic data can vary by ± 30%. The illustrative example below is based on the following assumptions:

- energy cost: € 0.08/kWh,
- cost of maintenance staff: € 25/h,
- cost of liquid waste destruction (concentrates and retentates): € 200/t,
- evaporator maintenance: 1 hour/day per evaporator, based on 240 days per year,
- membrane technique maintenance: 0.5 hour/day, based on 240 days per year.

b) Cost of treatment of typical acid/chromium effluents

For an acid/chromium effluent with a similar composition to that shown above, the configuration that would enable reuse of a distillate in production could involve:

- use of pH adjustment and chemical reduction,
- use of an evaporator with a suitable flow rate, made of appropriate materials (see above).

The evaporator flow rates required and the investment outlay and other costs are given below. The total cost of exploitation includes energy, maintenance, waste treatment, and consumables. Within the optimisation of this configuration, to reduce the size of the evaporators, and thus investment costs, pre-treatment using a combination of membrane techniques with a pH adjustment will be considered.

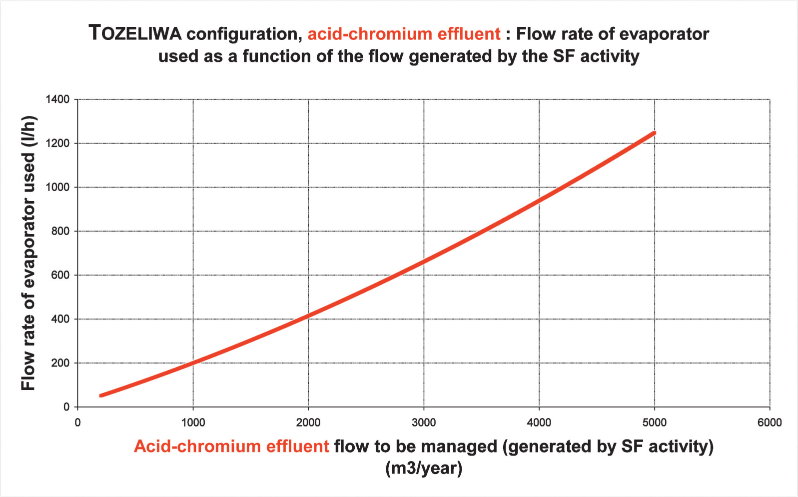


Figure 4.3. Acid-Chromium effluent: evaporator flow rate(L/h) as a function of flow to be managed (m^3/y)

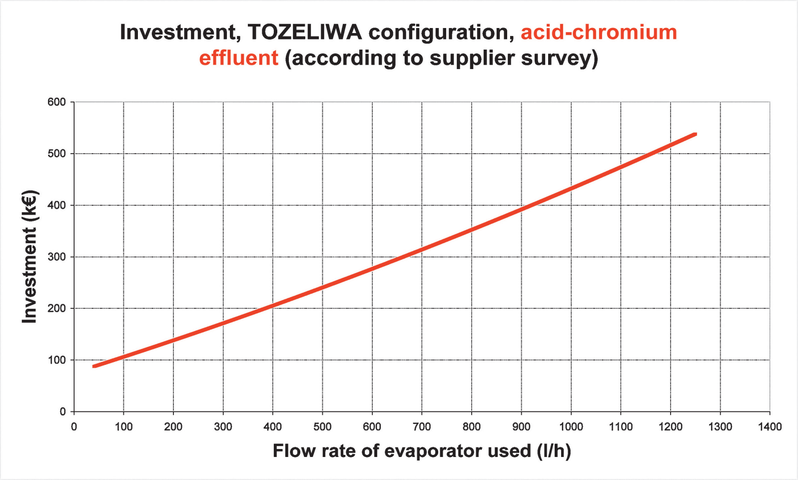


Figure 4.4. Acid-Chromium effluent: investment costs (k€) as a function of evaporator flow rate (L/h)

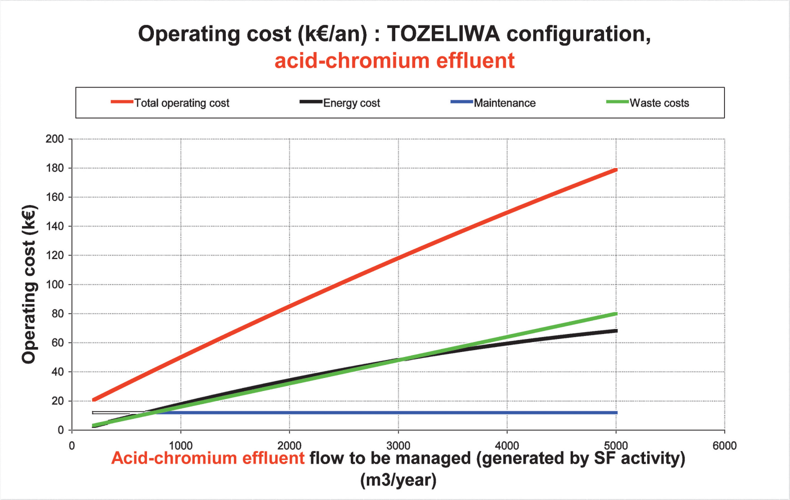


Figure 4.5. Acid-Chromium effluent: operating costs (k€/y) as a function of flow rate to be managed (m^3/y)

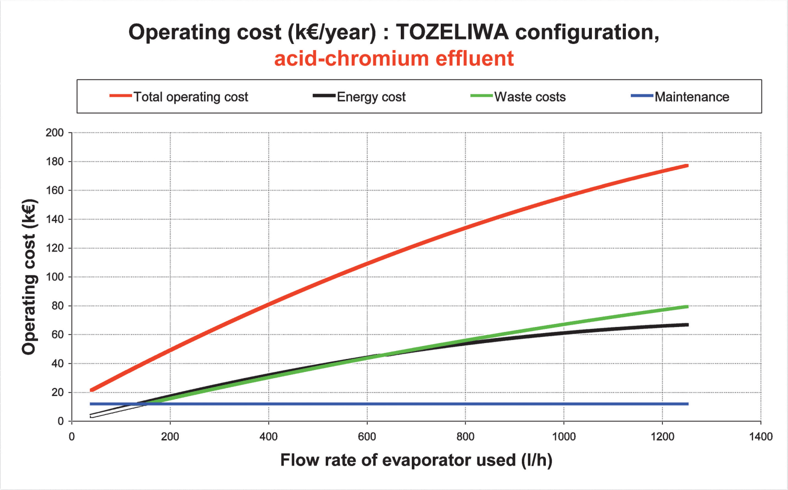


Figure 4.6. Acid-Chromium effluent: operating costs (k€/y) as function of evaporator flow rate (L/h)

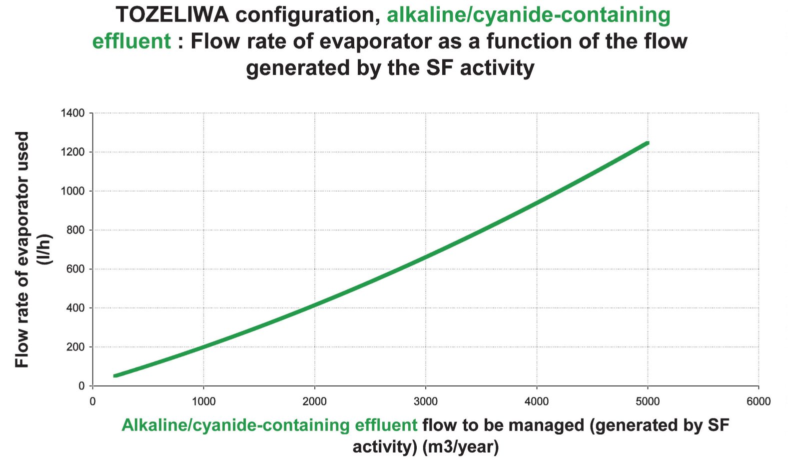


Figure 4.7. Alkaline-Cyanide effluent: evaporator flow rate (L/h) as a function of flow to be managed (m^3/y)

c) Cost of treatment of typical alkaline cyanide effluents

Using the same criteria as for the acid/chromium effluent of producing a distillate than can be reuse in production, and considering the introduction of pH adjustment, chemical oxidation and the use of an evaporator, the following data has been generated.

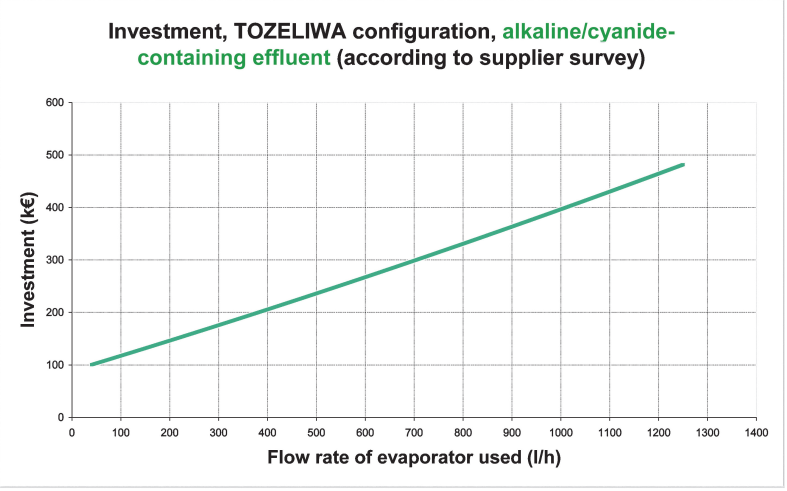


Figure 4.8. Alkaline-Cyanide effluent: investment costs (k€) as a function of evaporator flow rate (L/h)

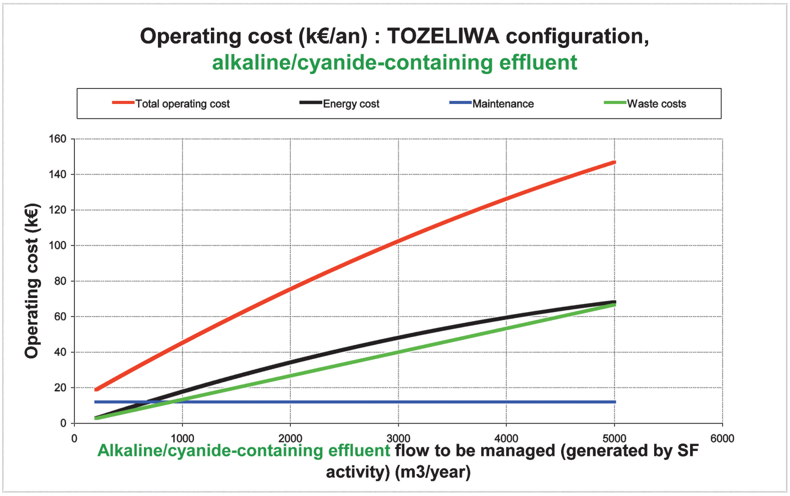


Figure 4.9. Alkaline-Cyanide effluent: operating costs (k€/y) as a function of flow rate to be managed (m^3/y)

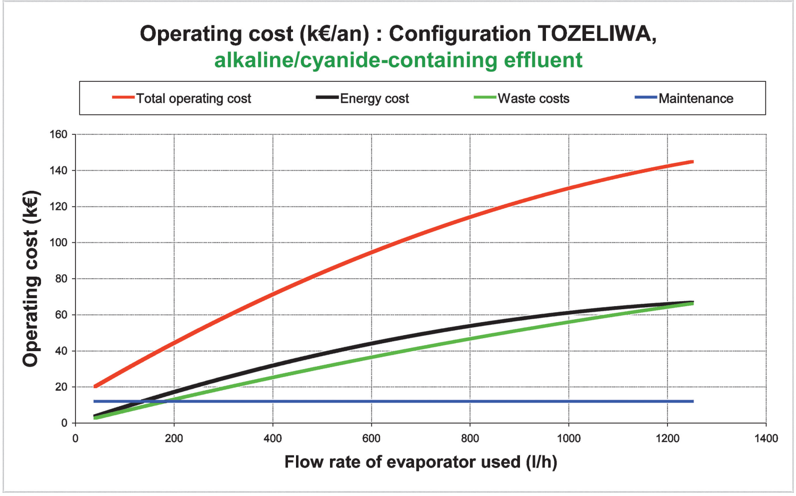


Figure 4.10. Alkaline-Cyanide effluent: operating costs (k€/y) as function of evaporator flow rate (L/h)

d) Cost of post-treatment

If the quality of the distillate is not suitable for recycle to the process plant, the treatment configuration has to take into account the addition of post-treatment processes. The techniques developed for this purpose use membranes (NF, RO) adapted to the composition and flow rate of the effluent.

The RO membrane area required, investment and other costs to be considered are given below. These costs must be added to those generated by the evaporator(s) used to treat the acid/chromium and/or alkaline/cyanide-containing effluents presented above.

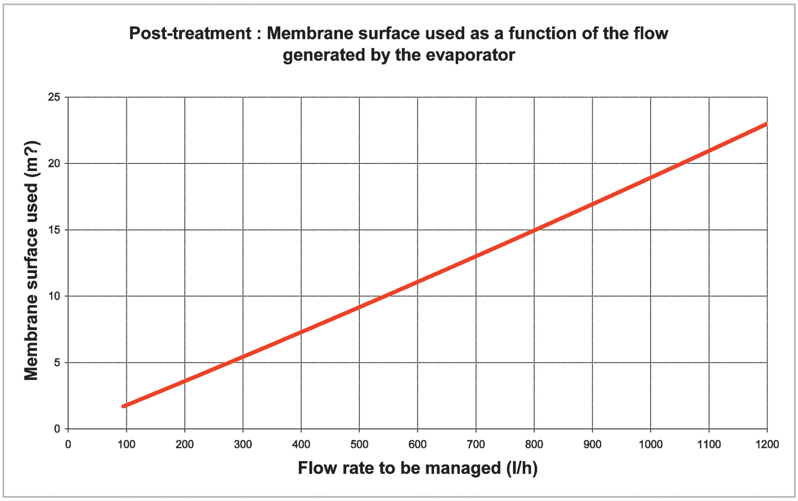


Figure 4.11. Post-treatment: membrane area (m^2) required as a function of effluent flow rate (L/h)

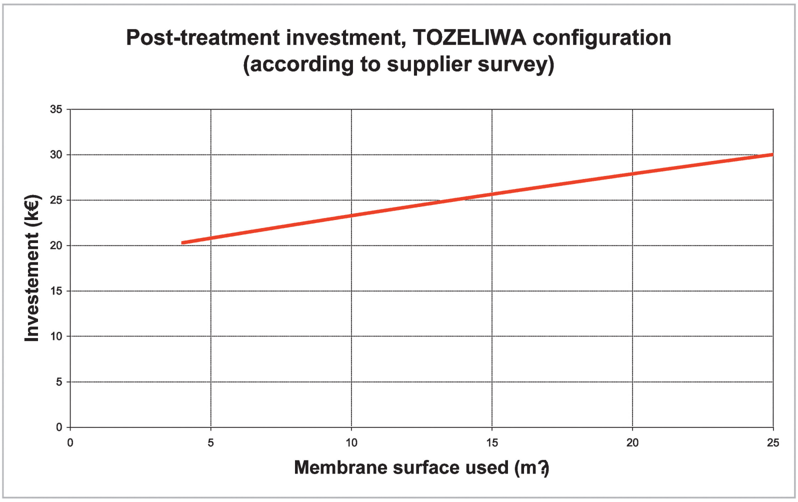


Figure 4.12. Post-treatment : investment cost (k€) as a function of membrane area (m^2)

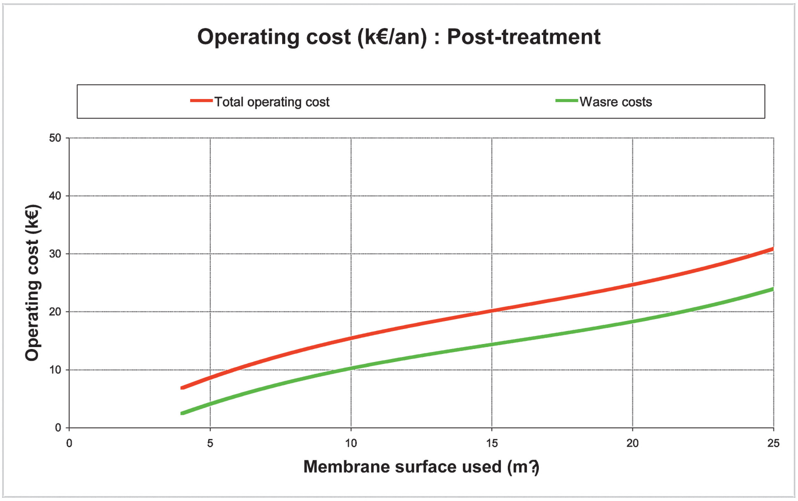


Figure 4.13. Post-treatment: total operating costs (k€) as a function of membrane area (m²)

e) Examples of application

Assuming that the overall flow rates of effluents from a surface treatment workshop *after implementation of "good practice"* are as follows:

- 2000 m^3/year of acid/chromium effluents,
- 2000 m^3/year of the alkaline/cyanide effluents,

and using the data provided above, an economic assessment is proposed for three hypothetical cases.

Case 1: <u>Treatment of acid/chromium effluents by evaporation</u>

Flow rate of the acid/chromic effluents: 2 000 m^3/year
Evaporator specifications capacity: 400 L/h; capital cost: 200 k€
Overall capital and operating costs on an annual basis:

Equipment	Capital cost (k€)	Operating costs (k€)			
		Energy	Maintenance	Waste	Consumables
Evaporator	200	35	12	30	8
Total	**200**	**85**			

Case 2: Treatment of the acid/chromic effluents by evaporation and post-treatment (membrane filtration)

Aim: to improve quality of distillate for reuse in process plant

Flow rate of the acid/chromic effluents: 2 000 m^3/year
Evaporator specifications capacity: 400 L/h; max. flow rate: 400 L/h; capital cost: 200 k€
Membrane filtration: membrane area: 7 m^2 ; capital cost: 22 k€
Overall capital and operating costs on an annual basis:

Equipment	Capital cost (k€)	Operating costs (k€)			
		Energy	Maintenance	Waste	Consumables
Evaporator	200	35	12	30	8
Membrane filtration	22	1	3	10	1
Total	**222**	**36**	**15**	**40**	**9**
TOTAL	**222**	**100**			

Case 3: Treatment of the alkaline/cyanide-containing effluents by evaporation

Flow rate of the alkaline/cyanide-containing effluents: 2 000 m^3/year
Evaporator specifications Capacity: 400 L/h; capital cost: 200 k€
Overall capital and operating costs on an annual basis:

Equipment	Capital cost (k€)	Operating costs (k€)			
		Energy	Maintenance	Waste	Consumables
Evaporator	200	30	12	25	3
Total	**200**	**70**			

f) Conclusions

The cleaner technology concept based on evaporation techniques in combination with or without membrane techniques is a technically feasible alternative to classical physico-chemical processes used to manage effluents generated by surface treatment activities.

Advantages include the possibilities offered in achieving “zero liquid discharge on-site” and thus environmental safety. The application of these technologies requires both the prior implementation of “good practice” to reduce flows generated by production processes, the definition of effluent flow characteristics (flow rate, composition), and the quality of recycle water required in the process. To these requirements must be added the use of specific evaporators appropriate for use with the effluents and the incorporation, if necessary, of preliminary and/or post-treatment operations, involving both investment outlay and operating costs.

IV.5. NEW PROMISING TECHNIQUES FOR THE FUTURE

IV.5.1. Electrochemical complexation-decomplexation of heavy metals

This process uses the complexation properties of some polymers (e.g. poly-4-vinylpyridine (P4VP)) grafted by electro-polymerisation on metallic supports with large specific surface areas (grilles). These grilles are then stacked into a cartridge shaped filter through which circulates the liquid containing the ions to be complexed. The grilles are polarised and the solution cations are fixed on the grilles with the double action from the complexing properties of the polymer and its electo-polarisation. At the exit a pure effluent is collected. The reaction can be reversed by inversion of the polarisation current.

Currently only some prototypes are running to treat baths containing copper and following treatment the effluent does not contain more than 0.1 ppm of copper.

Applications

The most interesting application in surface treatment industry is the purification of water from the plating of printed circuits.

Another potential application is the production of pure water for the preparation of electrolytic baths

IV.5.2. Biosorption

(for more information see Section 3).[2]

Many studies over the years have shown that tree and plant wastes, fungi, and bacteria can adsorb heavy metals from aqueous solution. The interest in this technique is the very low capital and operating costs. The adsorbed metals can be recovered by burning the spent waste material.

IV.5.2.1. Applications

This technique is applicable to reduce the metallic content of rinses and other waste-waters containing low concentrations of metals.

A prototype functioning with strips of papers allows fixing of the heavy metals and reduction of the concentration from 10g/L to 1g/L.

IV.5.2.2. Advantages

- potentially low cost, depending on source of biomass,
- good removal of heavy metals in effluents,
- easy monitoring,
- clean technology.

IV.5.2.3. Disadvantages

- size of equipment,
- paper strength.

Section 3

General Processes for the Treatment of Industrial Liquid Effluents

CONTENTS

I.

ADVANCED OXIDATION PROCESSES

INDEX

I.1. GENERAL PRINCIPLES

Advanced Oxidation Processes (AOP) have been widely explored for the decontamination of water polluted mainly by organic compounds. These processes are used to complete the degradation initiated by biological treatment or as a pre-treatment to enhance the biodegradability of recalcitrant or treatment-inhibiting compounds present in waste-waters. This enhancement is achieved by the partial oxidative degradation of the molecules to give intermediate reaction products that can be degraded by micro-organisms in a biological post-treatment.

A wide variety of advanced oxidation processes are available for waste-water treatment based on the photocatalytic systems: TiO_2/UV and Fe/UV-Visible, as well as reactions that produce hydroxyl radicals by the photolysis of hydrogen peroxide and ozone such as H_2O_2/UV, O_3/UV, and H_2O_2/O_3/UV.

Photocatalytic reactions can be divided into heterogeneous and homogeneous processes that use either catalyst particles or coatings such as TiO_2, or soluble catalysts or redox systems like iron ions or iron complexes. The necessary light energy can either be provided by lamps or solar radiation.

Heterogeneous photocatalysis (TiO_2/UV) and the homogeneous photo-Fenton (Fe/UV-Visible) processes are of special interest since sunlight can be used, while AOPs based on O_3 and H_2O_2 photolysis need shorter wavelength photons, which have to be generated by high-energy and expensive UV lamps. Solar irradiation combined with TiO_2 or Fe could represent an economic benefit for sunny countries where effluent discharge regulations are not too restrictive. The advantage of TiO_2 is that no additional chemicals are used but the absorption of the photocatalyst is limited to 385 nm therefore requiring at least a UV-A light and the overall process efficiency is much lower compared to the Photo-Fenton Treatment.

I.2. PHOTO-FENTON REACTION

This is identified as the most promising approach for the treatment of a wide range of organic contaminants in waste-water. It is a very powerful method of generating hydroxyl radicals described by a complex set of individual reactions involving iron (III) salts and hydrogen peroxide (Equations 1-4), of which the key step (Equation 1) is the photon induced production of hydroxyl radicals from water by the reduction of iron (III) to iron (II):

$$Fe_{aq}^{3+} \xrightarrow{h*v} {}^{*}Fe_{aq}^{3+} \rightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \tag{1}$$

These iron(II) ions then react with hydrogen peroxide forming further hydroxyl radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{2}$$

As a side-reaction some of the Fe(II) ions are oxidised by the hydroxyl radicals forming Fe (III) and hydroxide ions:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \tag{3}$$

There is another reaction between Fe(III) with hydrogen peroxide that also forms that forms radicals:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \tag{4}$$

The Fenton reaction was described towards the end of the 19th century, but its application to waste-water treatment was only developed in the second half of the last century and has now become very popular for the treatment of a wide range of contaminating organic compounds. If the Fenton reaction is irradiated with UV-Vis radiation it is called the ‘photo-assisted Fenton reaction’ or simply ‘photo-Fenton reaction’.

I.3. HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis is based on the use of a wide-band-gap semiconductor, where photo-excitement of a valence band electron leads subsequently to several reactions and production of the desired hydroxyl radical. The semiconductors are generally used in waste-water treatment either as a slurry or supported on suitable carrier materials. The oxidation reactions are initiated by irradiation of the photocatalyst with photons having higher energy than the band gap energy between valence and conductivity band of the semiconductor. The most intensively studied semiconductor for this purpose is titanium dioxide which has a band gap energy of around 3.2 eV, which means that the wavelength necessary to photo-excite an electron is 390 nm or shorter, which coincides with the border region between ultraviolet and visible radiation.

By absorbing a UV photon, charge separation occurs and an electron is promoted into the conductivity band while a positively charged electron hole remains in the valence band (Equation 5).

$$TiO_2 + h\nu \xrightarrow{k\,f} e^{-} + h^{+} \tag{5}$$

Subsequently, the electron and the electron hole can recombine dissipating thermal energy (Equation 6),

$$e^{-} + h^{+} \xrightarrow{k_R} energy \tag{6}$$

or the electron can react with dissolved oxygen (Equation 7), whereby the electron hole is stabilised,

$$e^{-} + O_2 \xrightarrow{k_{O_2}} {}^{\bullet}O_2^{-} \tag{7}$$

or the electron hole reacts with adsorbed hydroxyl ions (Equation 8),

$$h^{+} + OH^{-} \xrightarrow{k_{^\bullet OH}} {}^{\bullet}OH \tag{8}$$

or directly with adsorbed organic species (Equation 9).

$$h^{+} + R \xrightarrow{k_{O}} R_{1} \tag{9}$$

The overall Photo-Fenton treatment can be summarised overall by equations 10-13 with equation 10 showing the most important reactions involving iron and hydrogen peroxide

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}} \tag{10}$$

Ferric iron complexes can be photolysed upon irradiation via a ligand-to-metal charge transfer reaction by passing through a photo-excited transition state before charge transfer and complex dissociation happens (Equation 11).

$$\mathrm{[Fe^{3+}L] + h\nu \rightarrow [Fe^{3+}L]^{\bullet} \rightarrow Fe^{2+} + {}^{\bullet}L} \tag{11}$$

The photolysis of ferric iron/aquo complexes should be specially mentioned as apart from efficiently regenerating ferrous iron also generates further hydroxyl radicals (Equation 12).

$$\mathrm{[Fe^{3+}(OH^{-})_x(H_2O)_y] + h\nu \rightarrow Fe^{2+} + (x\text{-}1)OH^{-} + yH_2O + {}^{\bullet}OH} \tag{12}$$

Ferric iron/ carboxylic acids complexes can also be photolysed with often very high quantum yields and also with wavelengths up to around 580 nm. As a result ferrous iron regeneration and pollutant decarboxylation take place (Equation 13).

$$\mathrm{[Fe^{3+}(RCO_2^{-})] + h\nu \rightarrow Fe^{2+} + {}^{\bullet}R + CO_2} \tag{13}$$

There is a big difference between using Fe^{2+} or Fe^{3+} at the beginning of the process in the dark, but not under illumination. If the Photo-Fenton reaction is performed at low iron concentration, which is often very useful, mainly for simplifying iron removal at the end of the process and/or for treating the water in a subsequent biological treatment without removing iron, the decision between the use of the two iron oxidation states should be taken only for economical reasons (price of iron salts).

References

J J Pignatello, E Oliveros and A MacKay, *Advance Oxidation Processes for Organic Contaminant Destruction based on the Fenton reaction and Related Chemistry*, Crit. Rev. Environ. Sci. Technol. **36**, 1-84, (2006)

P R Gogate and A B Pandit, *A review of Imperative Technologies for Wastewater Treatment I: Oxidation technologies at ambient conditions*. Adv. Env. Res. **8**(3-4), 501-551, (2003)

P R Gogate and A B Pandit, *A review of imperative technologies for wastewater treatment II: hybrid methods,* Adv. Env. Res. **8**(3-4), 553-597, (2004)

E Neyens and J Baeyens, *A review of classic Fenton's peroxidation as an advanced oxidation technique,* J. Hazard. Mat. **98**(1-3), 33-50, (2003)

K Ikehata and M G El-Din, *Degradation of recalcitrant surfactants in wastewater by ozonation and advances oxidation processes: A review*, Ozone-Sci. Eng. **26**(4), 327-343, (2004)

D Mantzavinos and E Psillakis, *Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment*, J. Chem. Tech. Biotechnol. **79**(5), 431-454, (2004)

II.

BIOPROCESSING - PRINCIPLES AND APPLICATIONS FOR METAL IMMOBILIZATION FROM WASTE-WATER STREAMS

INDEX

II.1. PRINCIPLES OF BIOSORPTION

Biosorption can be defined as the selective sequestering of metal soluble species that result in the immobilization of the metals by microbial cells. It refers to physicochemical mechanisms of inactive (i.e. non-metabolic) metal uptake by microbial biomass.[16] Metal sequestering by different parts of the cell can occur via various processes: complexation, chelation, coordination, ion exchange, precipitation, reduction.[8,16,17,21,24,26,27,28,53,62,63,64] Immobilization may be the result of more than one mechanism, for example, metal complexation may be followed by metal reduction or metal precipitation.

Metabolically active and inactive cells behave in different ways. Thus inactive microbial cells can only immobilize metals by biosorption, whereas active microbial cells may immobilize soluble metal species both by biosorption and by other mechanisms that are part of and/or are due to the microbial metabolism.[23, 34, 60]

II.2. BIOSORPTION SITES

The cell wall is usually the first cellular structure that comes in contact with the soluble metal species in the extracellular environment, if the possibility of interaction and retention of metal species by extracellular excretions produced by some microbial cells is excluded.

A microbial cell wall is a well-defined polymeric matrix located just outside the plasma membrane of a cell. Cell walls provide increased mechanical strength and resistance and can be composed of polysaccharides, proteins, lipids, or a combination of these compounds. They are part of the structure of eubacteria, archaebacteria, fungi, algae, and plants.

Almost all eubacterial species have cell walls containing a polysaccharide called peptidoglycan. Among the eubacteria, differences in cell wall structure are a major feature used in classifying these organisms into two main groups: Gram Positive and Gram Negative bacteria.

The cell walls of archaebacteria are distinctive from those of eubacteria being composed of different polysaccharides and proteins, with no peptidoglycan. Many archaebacteria have cell walls made of the polysaccharide pseudomurein.

Fungal cell walls are typically composed of the polysaccharides chitin and cellulose, and the cell walls of algae and plants are composed mainly of the polysaccharide cellulose.

Proteins, polysaccharides and nucleic acids[4,5,19,25,42,56] are the three major polymer groups ubiquitous in the living world, being found in all members of the animal, plant, protozoan and microorganism groups.

These biopolymers, constituents of the cell wall and the other parts of the cell possess functional groups that have a significant potential for metal binding.[11, 19, 25, 41, 42] Furthermore, intracellular biopolymers such as proteins and DNA may also contribute to metal immobilisation. In many cases, extracellular polymeric substances such as Exo-PolySaccharides (EPS) that are closely related to the cell membrane can also participate in metal immobilisation.[12]

As a generalization, the binding of metal ions to biopolymers is likely to be via two major mechanisms, the first of these being simple ion-exchange and the second through the formation of complexes (co-ordination compounds) which may be chelates. Because of the complexity of most biopolymers, it is very likely that more than one processes of binding take place in a system at the same time. Two simplified examples are:

- metal-ion exchange: via cation-binding with ionisable functional groups found in biopolymers such as carboxyl, organic phosphate and organic sulfate,
- complex formation by organic molecules (ligands) with metal atoms: where one or more lone electron pairs of the ligand are donated to the metal. The most likely electron donor atoms in biopolymers are neutral trivalent nitrogen atoms and neutral divalent oxygen or sulfur atoms.

II.3. BIOSORPTION MECHANISMS

The elucidation of the mechanism of biosorption is necessary to enable the technology to be developed.[46, 47, 52] Such mechanisms are complicated[57-59] and not fully understood. An extensive literature exists concerned with the mechanism and modeling of biosorption referring to specific elements and microbial strains.[32, 33, 45, 48, 50, 51, 55] The key factors controlling and characterizing these mechanisms are:

- the type of biological ligands available for metal sequestering,
- the status of the biomass, i.e. living /non-living,
- the chemical, stereochemical and coordination characteristics of the targeted metals and metal species,[35, 44]
- the characteristics of the metal solution such as pH and the presence of competing co-ions.[18, 20, 22, 39, 40, 43]

Microorganisms possess an abundance of functional groups that can passively adsorb metal ions. The term adsorption can be used as a general term and includes several passive, i.e. non-metabolic, mechanisms such as: complexation; chelation; co-ordination; ion exchange; precipitation; reduction (Figure 3.1).

II.3.1. Complexation

As noted above complex formation of metal ions with organic molecules involves ligand centres in the organic species i.e. the presence of an atom or atoms having lone pair electrons to donate.

Complexation may be electrostatic or covalent and the simplest case is complexation by a monodentate ligand such as RNH_2.

To approach and elucidate biosorption mechanisms, a significant part of the recent advances in biosorption are based on the classification of elements according to the hard-soft acid-base classification (Pearson's classification). "Hard acids", metals such as Na, K, Ca, Mg, often essential nutrients for microbial growth, bind preferentially to oxygen-containing "hard bases", ligands such as OH^-, HPO_4^{2-}, CO_3^{2-}, $R\text{-}COO^-$, and =C=O.

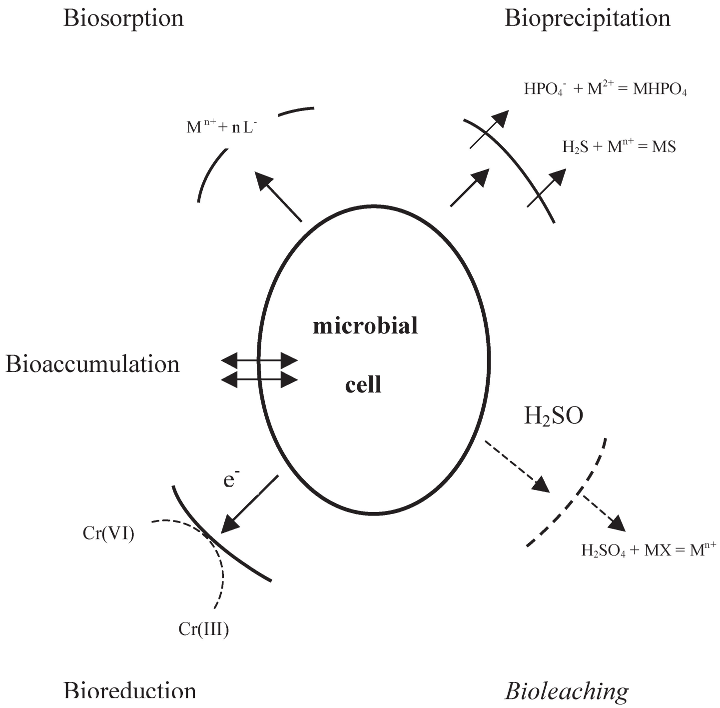


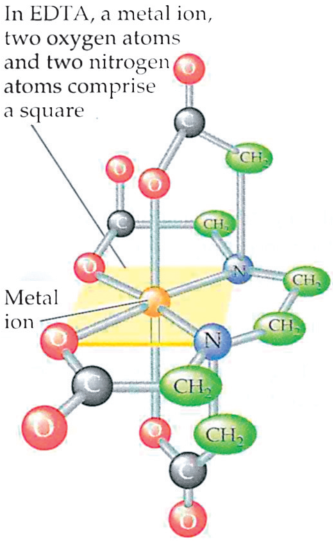
Figure 3.1. Interactions between metal ions and microbial cells

Soft acids, metals such as the precious metals Ag, Au, Pt, Pd are bound covalently to the cell wall by "soft bases", ligands containing nitrogen or sulfur. As noted earlier several mechanisms might be involved in the immobilisation of metals and it is now evident and confirmed by several researchers, that the biosorption of precious metals is a two step mechanism comprising first covalent bonding and then *in-situ* reduction.[4, 5, 35, 44]

Borderline ions on the "hard/soft" classification such as the transition elements: Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} exhibit a significant degree of covalent bonding with nitrogen or sulfur containing "soft" ligands.[1, 6]

II.3.2. Chelation

Organic molecules containing more than one functional group with donor electron pairs can simultaneously donate these to a metal atom. This can result in the formation of a ring structure involving the metal atom a process termed ‘chelation’. Figure 3.2 shows the structure of a metal ion chelated with ethylenediamine tetracarboxylic acid (EDTA), a hexa-donating compound with two nitrogen and four oxygen donor atoms.


In EDTA, a metal ion, two oxygen atoms and two nitrogen atoms comprise a square

Metal ion

Figure 3.2. Schematic diagram of bonding in a metal-EDTA complex ion

In general, since a chelating agent may bond to a metal ion in more than one place simultaneously, chelated compounds are more stable than complexes involving mono-dentate ligands. Stability tends to increase with the number of chelating sites available on the ligand. Thus chelation of metals by donor ligands of biopolymers leads to the formation of stable species.

II.3.3. Co-ordination

Metal atoms have preferences for specific donor atoms (“hard/hard” / “soft/soft”) and the stereochemical arrangements that play an important role in the binding with the available ligands on the microbial cell. Limited information of surface complexation models, based on the theory of surface co-ordination chemistry, is available to describe metal biosorption; however the preferences of the metal species should be considered to explain observed metal biosorption capacities and to elucidate biosorption mechanisms.[35, 44]

II.3.4. Ion exchange

The gram-positive bacteria, principally members of the genus *Bacillus,* have enhanced capacity for metal binding because of a significant negative charge density[16, 63, 64] This is due to the structure of the cell wall with teichoic and teichuronic acids attached to the peptidoglycan network. The phosphodiesters of teichoic acid and the carboxylate groups of the teichuronic acid thus contribute ion-exchange capacity to the cell wall.

Cation Exchange

So far as metal ion-exchange is concerned, in biopolymers the most likely cation binding ionisable groups to be involved, are: carboxyl, organic phosphate and organic sulfate.

Carboxylic acids are widely distributed in biopolymers being most commonly found as side-chain constituents of proteins, the uronic, neuraminic and muramic acids, and related substituted monosaccharides of polysaccharides.

Phosphodiester links impart negative charge to the nucleic acid backbone (Figure 3.3) while both diester and monoester groupings are found most commonly in bacterial polysaccharides and related macromolecules. Lipoprotein and lipopolysaccharides are also likely to contain phosphodiester as part of the lipid moiety.

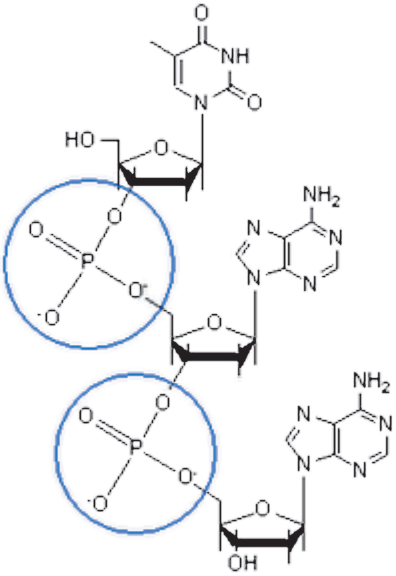


Figure 3.3. Phosphodiester structure (circled)

Sulfate esterified to carbohydrate hydroxyl groups is common in connective tissue and algal polysaccharides and is for most purposes likely to provide the greatest negative charge density, at very low pK_a, among the charged biopolymers. Ester sulfate and phosphomonoester groupings also occur in proteins.

Hydroxyl groups of serine, threonine and tyrosine are available for specific translational modifications. Phenolic hydroxyl is also capable of providing weak negative charge and binding potential.

Anion Exchange

Anion exchange on biopolymers can take place on a variety of organic-nitrogen-based groupings. In proteins, amino (lysyl side chain and N-terminal) imidazole (histidyl) and guanidine (arginyl) groupings are common centres of positive charge. Centres of positive charge in nucleic acids will occur with protonation of amino groups on purine or pyrimidine rings or with protonation of heterocyclic nitrogen atoms.

Polysaccharides as a group are acidic or neutral macromolecules with basic functional groups being rare and arising as un-acetylated aminosugars. Chitin is the notable example where a proportion of glucosamine residues are reportedly un-acetylated and which provides on deacetylation chitosan with a high proportion of protonisable positive charge centres.

Many examples have established the existence of an ion exchange mechanism in metal ion removal by biosorption.[10, 36, 61, 62] However, it has been suggested by many researchers that ion exchange is neither the sole nor the main mechanism for metal biosorption.[6]

II.3.5. Precipitation

Metal precipitation is also involved in biosorption. The precipitates may be formed and remain in contact with or inside the microbial cells or may be independent of the solid phase of the microbial cell. In the later case, the presence of the solid phase-microbial cell or biofilm also plays a favourable role in the phenomenon of precipitation.

The term precipitation in most cases refers to the formation of insoluble inorganic metal precipitates.[30,31] However, in the case of metal biosorption by microbial cells, organic metal precipitates may also be formed. This may be more easily understood when metals are bound to Extracellular Polymeric Substances (EPS) excreted by some prokaryotic (bacteria, archaea) and eukaryotic (algae, fungi) microorganisms. Purified products from isolated cells such as glucan, mannan, and chitin accumulate greater quantities of cations than the intact cells, proving that biomolecules can form metal precipitates.

II.3.6. Reduction

The removal of toxic hexavalent chromium from aqueous solution by biosorption by different biomass types has been extensively reported. This removal is often associated with the simultaneous reduction of Cr(VI) to Cr(III), thus inactivated fungal biomass e.g. *Aspergillus niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae* and *Penicillium chrysogenum* remove Cr(VI) from aqueous solutions by reduction to Cr(III) when contacted with the biomass.[13-15]

Also soft metals like gold and palladium are first bound on sites on and within the cell wall and these sites act as nucleation points for the reduction of metals and growth of crystals and elemental gold and palladium have been obtained. The biosorption mechanism is a two-step process: initiation of the uptake at discrete points by chemical bonding, then reduction of the metal ions.[4, 5, 29, 35]

II.4. APPLICATIONS OF BIOSORPTION

Pilot installations and few commercial scale units were constructed in the USA and Canada during 1980s and 1990s, (Table 3.1). These pilot plants confirmed the applicability of biosorption as a basis for metal sequestering/recovery processes especially in the case of uranium. Here it was tested as an integral part with *in situ* bioleaching, of a biotechnologically based uranium production scheme.[37]

These pilot plants helped researchers realize the limitations associated with using biosorption with inactive microbial biomass in an industrial application, mainly due to the cost of formulating the biomass into an appropriate biosorbent material. Furthermore, the negative effect of co-ions in the solution on the uptake of the targeted metals by the immobilized microbial biomass, and the reduced resilience of the biological material, made recycling and reuse of the biosorbent even more difficult.[39]

Biosorption however is a process with some unique characteristics. It can effectively sequester dissolved metals from very dilute complex solutions with high efficiency. This makes biosorption an ideal candidate for the treatment of high volume low concentration complex waste-waters. Moreover, it has recently been shown that in cases of metabolically active microbial cells, in biological reactors, biosorption contributes as a parallel mechanism together with other metabolically mediated mechanisms such as bioprecipitation and bioreduction.[23] For this reason, biosorption should always be taken into account as a metal immobilization process in every case of metal bearing water streams treatment technology based on the interactions of microbial cells with soluble metal species.

Name	Microorganism	Immobilization matrix	Particle size (mm)	Ref.
Bio-fix U.S. Bureau of Mines, (Golden, Colorado)	Cyanobacteria (*Spirulina*); Yeast; Algae; Plants (*Lemna* sp., *Sphagnum* sp.)	polyethylene or polypropylane or polysulfone in dimethylformamide	0.5-2.5	3
AMT-Bioclaim	*Bacillus subtilis*			7
AlgaSORB™ Bio-recovery System Inc. (Las Cruces, New Mexico)	*Chlorella vulgaris*	silica or polyacrylamide gels		2, 9

Name	Microorganism	Immobilization matrix	Particle size (mm)	Ref.
B.V.Sorbex Inc., (Montreal, Canada)	*Sargassum natans;* *Ascophyllum nodosum;* *Halimeda opuntia;* *Palmyra pamata ;* *Chondrus crispus;* *Chlorella vulgaris*			63
Tsezos (Greece)	*Rhizopus arrhizus;* Activated sludge; P. chrysogenum	polymer coating	0.5-1.0	49

Table 3.1. Biological based sorbent particles (Biosorbents) developed for metal bearing waste-water treatment[32]

The management of the solid waste produced by the biosorption of metal ions on the microbial cells should be considered according to the characteristics of the treatment procedure and the metals sorbed. Thus if the microbial cells are immobilized in a chemical matrix with the sorbent particles, then the desorption of metals is the only method of making the process economically sound, independent of the value of the metals to be recovered. Also in the case of naturally forming biofilms the excess sludge should be treated appropriately. Usually the metals are recovered by leaching with a desorbing agent, such as dilute acid or chelating compounds. But if metal recovery is not economically interesting, the loaded biomass is treated according to the safety regulations for sludge disposal after dewatering or drying.

References

1. S V Avery and J M Tobin, *Mechanism of adsorption of hard and soft metal ions to Saccharomyces cerevisiae and influence of hard and soft anions,* Appl. Environ. Microbiol. **59**, 2851-2856, (1993).
2. G W Bedell and D W Darnall, *Immobilization of nonviable biosorbent algal biomass for the recovery of metal ions,* in Biosorption of Heavy Metals, B Volesky, (ed)., CRC Press, Boca Raton, La. Pp 313-326, (1992)
3. P G Bennett, C R Ferguson and T H Jeffers, *Biosorption of metal contaminants from acidic mine waters,* Process Mineralogy XI - Characterization of Metallurgical and Recyclable Products, D M Hausen, W Petruk, R D Hagni and A Vassiliou, (eds), pp 213-222, (1991).
4. T J Beveridge and R G E Murray, *Uptake and retention of metals by cell walls of Bacillus subtilis,* J. Bacteriol, **127**, 1502-1518, (1976).
5. T J Beveridge and R G E Murray, *Sites of metal deposition in the cell wall of Bacillus subtilis,* J. Bacteriol, **141**, 876-883, (1980).

References

6. J M Brady and J M Tobin, *Binding of hard and soft metal ions to Rhizopus arrhizus biomass,* Enzyme and Microbial Technology **17**(9), 791-796, (1995)
7. J A Brierley, *Production and application of a Bacillus-based product for use in metals biosorption*, in Biosorption of Heavy Metals, B. Volesky (ed), CRC Press, Boca Raton, La. pp 305-311, (1990).
8. K Chandra Sekhar, S Subramanian, J M Modak and K A Natarajan, *Removal of metal ions using an industrial biomass with reference to environmental control,* Int. J. Min. Proc., **53** (1-2), 107-120, (1998).
9. D W Darnal, B H Green, R A McPherson, M Henzl, and M D Alexander *Recovery of heavy metals by immobilized algae*, in Trace Metal Removal from Aqueous Solution, Thompson (ed), The Royal Society of Chemistry, pp 1-24, (1986).
10. T A Davis, B Volesky and A Mucci, *A review of the biochemistry of heavy metal biosorption by brown algae,* Water Res., **37**(18), 4311-4330, (2003)
11. L Diels, M Tsezos, T Pümpel, B Pernfuss, F Schinner, A Hummel, L Echard and F Glombitza, *Pseudomonas mendocina AS302 a bacterium with a non selective and very high metal biosorption capacity*, in Biohydrometallurgical Processing, C A Cerez, T Vargas, H Toledo and J V Wiertz (eds.), University of Chile, pp.195-200, (1995)
12. L Diels, P Corbisier, L Hooyberghs, F Glombitza, A Hummel, M Tsezos, T Pümpel, B Pernfuss, F Schinner and M Mergeay, *Heavy metal resistance and biosorption in Alcaligenes Eutrophus ER 121,* in Biohydrometallurgical Processing C A Cerez, T Vargas, H Toledo and J V Wiertz (eds.), University of Chile, pp.287-297, (1995)
13. Donghee Park, Yeoung-Sang Yun and Jong Moon Park, *Studies on hexavalent chromium biosorption by chemically-treated biomass of Ecklonia sp.,* Chemosphere, **60**(10), 1356-1364, (2005)
14. Donghee Park, Yeoung-Sang Yun and Jong Moon Park, *Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics,* Process Biochem., **40** (7), 2559-2565, (2005).
15. Donghee Park, Yeoung-Sang Yun, Ji Hye Jo and Jong Moon Park, *Mechanism of hexavalent chromium removal by dead fungal biomass of Aspergillus niger,* Water Res., **39**(4), 533-540, (2005)
16. H Eccles and S Hunt, Immobilisation of Ions by Bio-Sorption, Ellis Horwood Ltd. Chichester, U.K. (1986).
17. H Eccles, *Treatment of metal-contaminated wastes: why select a biological process?* Trends in Biotechnol., **17**(12), 462-465, (1999)
18. A Esposito, F Pagnanelli and F Vegliò, *pH-related equilibria models for biosorption in single metal systems,* Chem. Eng. Sci., **57**(3), 307-313, (2002)
19. H-C Flemming, *Sorption sites in biofilms,* Water Sci. Technol. **32**(8), 27-33, (1995).
20. E Fourest, C Canal and J-C Roux, *Improvement of heavy metal biosorption by mycelial dead biomasses (Rhizopus arrhizus, Mucor miehei and Penicillium chrysogenum): pH control and cationic activation,* FEMS Microbiology Reviews, **14**(4), 325-332, (1994)

References

21. M G Gadd, *Microbial Influence on Metal Mobility and Application for Bioremediation,* Geoderma, **122**(1-2), 109-119, (2004).
22. E Guibal, C Roulph and P Le Cloirec, *Uranium biosorption by a filamentous fungus Mucor miehei pH effect on mechanisms and performances of uptake,* Water Res., **26**(8), 1139-1145, (1992)
23. A Hatzikioseyian, E Remoudaki, and M Tsezos, *Biosorption and biological reduction of chromium by microbial biomass in batch and pilot scale rotating biological contactor (RBC),* in Proceedings of International Biohydrometallurgy Symposium IBS 2001; Biohydrometallurgy Fundamentals, Technology and Sustainable Development, Part B, V S T Ciminelli and O Garcia Jr., (eds.) pp 265-277, (2001).
24. Jianlong Wang and Chen Chan, *Biosorption of heavy metals by Saccharomyces cerevisiae : a review,* Biotechnology Advances, (2006) In Press
25. A Kapoor and T Viraraghavan, *Heavy metal biosorption sites in Aspergillus niger,* Bioresource Technology, **61**(3), 221-227, (1997).
26. A Kapoor and T Viraraghavan, *Fungal biosorption — an alternative treatment option for heavy metal bearing wastewaters: a review,* Bioresource Technol., **53**(3), 195-206, (1995)
27. D Kratochvil and B Volesky, *Advances in the biosorption of heavy metals,* Trends in Biotechnology, **16**(7), 291-300, (1998)
28. M Ledin and K Pedersen, *The environmental impact of mine wastes – Roles of microorganisms and their significance in treatment of mine wastes*, Earth – Science Rev. **41**, 67-108, (1996).
29. Zhongyu Lin, Chaohui Zhou, Jianming Wu, Jianzhang Zhou and Lin Wang, *A further insight into the mechanism of Ag^+ biosorption by Lactobacillus sp. strain A09,* Spectrochimica Acta Part A: Mol. Biomol. Spectro., **61**(6), 1195-1200, (2005).
30. L E Macaskie, R M Empson, A K Cheetham, C P Grey and A J Skarnulis, *Uranium bioaccumulation by Citrobacter sp. as a result of enzymatically growth of HUO_2PO_4,* Science, **257**, 784-789, (1992).
31. L E Macaskie, K M Bonthrone and D A Rauch, *Phosphatase-mediated heavy metal accumulation by Citrobacter sp. and related enterobacteria,* FEMS Microbiology Letters, **121**, 141-146, (1994).
32. F Pagnanelli, F Beolchini, A Esposito, L Toro and F Vegliò, *Mechanistic modeling of heavy metal biosorption in batch and membrane reactor systems,* Hydrometallurgy, **71**(1-2), 201-208, (2003).
33. F Pagnanelli, A Esposito and F Vegliò, *Multi-metallic modelling for biosorption of binary systems,* Water Res. **36**(16), 4095-4105, (2002).
34. R Pujol and J P Canler, *Biosorption and dynamics of bacterial populations in activated sludge,* Water Res. **26**(2), 209-212, (1992).
35. E Remoudaki, M Tsezos, A Hatzikioeyian and V Karakoussis, *Mechanism of palladium biosorption by microbial biomass. The effects of metal ionic speciation and solution co-ions,* Proceedings of Int. Biohydrometallurgy Symp. IBS 99: Biohydrometallurgy and the Environment toward the mining of the 21st Century Part B, R Amils and A Ballester (eds), Elsevier, pp 449-462, (1999).

References

36. I A H Schneider, J Rubio and R W Smith, *Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation?* Int. J. Miner. Process **62**, 111-120, (2001).
37. M Tsezos, *Biosorption of metals. The experience accumulated and the outlook for technology development,* Hydrometallurgy*,* **59**, 241-243, (2001).
38. M Tsezos, E Remoudaki and A Hatzikioseyian, *Emerging biotechnology applications in large scale treatment of metals bearing waste waters,* Proc. Fifth Int. Symp. on Environmental Issues and Waste Management in Energy and Mineral Production, (SWEMP'98), Ankara, Turkey, pp 665-671, (1998).
39. M Tsezos, Z Georgousis and E Remoundaki, *Mechanism of Aluminum Interference on Uranium Biosorption by Rhizopus arrhizus*, Biotechnol. Bioeng. **55**, 16-26, (1997)
40. M Tsezos, Z Georgousis and E Remoundaki, *Ionic Competition Effects in a Continuous Uranium Biosorptive Recovery Process,* J. Chem. Tech. Biotechnol., **70**, 198-206, (1997)
41. M Tsezos and E Remoundaki, *Recent advances in the mechanistic understanding of metals mobility and interaction with microbial biomass,* Research in Microbiol.*,* **148**, 515-517, (1997)
42. M Tsezos, E Remoundaki and V Angelatou, *Biosorption Sites of Selected Elements Using Electron Microscopy,* Comparative Biochemistry and Physiology, **118**, 481-487, (1997)
43. M Tsezos, E Remoundaki and V Angelatou, *A Study of the Effects of Competing Ions on the Biosorption of Metals, Int. Biodeter. Biodegrad.,* **38**, 19-29, (1996)
44. M Tsezos, E Remoundaki and V Angelatou, *A Systematic Study on Equilibrium and Kinetics of Biosorptive Accumulation. The Case of Ag and Ni,* Int. Biodeter. Biodegrad.*,* **35**, 129-153, (1995)
45. M Tsezos and A Deutschman, *The Use of a Mathematical Model for the Study of Important Parameters in Immobilized Biomass Biosorption*, J. Chem. Tech. Biotechnol., **53**, 1-12, (1992)
46. M Tsezos and A Deutschman, *An Investigation of Engineering Parameters for Use of Immobilized Biomass Ps in Biosorption*, J. Chem. Tech. Biotechnol., **48**, 29-39, (1990)
47. M Tsezos, R G L McCready and J P Bell, *The Continuous Recovery of Uranium from Biologically Leached Solutions Using Immobilized Biomass*, Biotechnol. Bioeng., **34**, 10-17, (1989)
48. M Tsezos, S H Noh and M H I Baird, *A Batch Reactor Mass Transfer Kinetic Model for Uranium Biosorption Using Immobilised Biomass Biosorption*, Biotechnol. Bioeng., **32**, 545-553, (1988)
49. M Tsezos, M H I Baird and L W Shemilt, *The Use of Immobilised Biomass to Remove and Recover Radium from Elliot Lake Uranium Tailings Streams*, Hydrometallurgy, **17**, 357-368, (1987)
50. M Tsezos, M H I Baird and L W Shemilt, *The Elution of Radium Adsorbed by Microbial Biomass,* Chem. Eng. J., **34**, B57-B64, (1987)

References

51. M Tsezos, M H I Baird and L W Shemilt, *The Kinetics of Radium Biosorption,* Chem. Eng. J., **33**, B35-B41, (1986)
52. M Tsezos, M H I Baird and L W Shemilt, *Adsorptive Treatment with Microbial Biomass of Ra-226 Containing Waste Waters*, Chem. Eng. J., **32**, B29-B38, (1986)
53. M Tsezos, *Selective Extraction of Metals from Solution by Microorganisms. A Brief Overview***,** Can. Metall. Quart., **24**, 141-144, (1985)
54. M Tsezos, and S H Noh, *Extraction of Uranium from Sea Water Using Biological Origin Adsorbents,* Can. J. Chem. Eng., **62**, 559-561, (1984)
55. M Tsezos, *Recovery of Uranium from Biological Adsorbents. Desorption Equilibrium,* Biotechnol. Bioeng., **26**, 973-981, (1984)
56. M Tsezos, *The Role of Chitin in Uranium Adsorption by Rhizopus Arrhizus* Biotechno. Bioeng., **25**, 2025-2040, (1983)
57. M Tsezos and B Volesky, *The Mechanism of Thorium Biosorption by R. arrhizus* Biotechnol. Bioeng., **24**, 955-969, (1982)
58. M Tsezos and B Volesky, *The Mechanism of Uranium Biosorption by* R. arrhizus Biotechnol. Bioeng., **24**, 385-401, (1982)
59. M Tsezos and B Volesky, *Biosorption of Uranium and Thorium,* Biotechnol. Bioeng., **23**, 583-604, (1981)
60. R F Unz and K L Shuttleworth, *Microbial mobilization and immobilization of heavy metals,* Current Opinion in Biotechnology*,* **7**(3), 307-310, (1996)
61. P Vasudevan, V Padmavathy and S C Dhingra, *Biosorption of monovalent and divalent ions on baker's yeast,* Bioresource Technol., **82**(3)*,* 285-289, (2002)
62. F Veglio and F Beolchini, *Removal of metals by biosorption: a review.* Hydrometallurgy **44**, 301-316, (1997)
63. B Volesky, Biosorption of Heavy Metals, CRC Press, Boca Raton, Fa, (1990).
64. J Wase and C Forster, Biosorbents for Metal Ions, Taylor and Francis, Ltd, (1997)

III.

EVAPORATION

INDEX

III.1. INTRODUCTION

Evaporation is a thermal process that permits the separation of a solution into two phases: a distillate composed of practically pure solvent and a concentrated residual phase containing the solid contents of the original solution. This possibility of separating the phases by a simple physical means has numerous industrial applications. The following discussion will focus on the treatment of aqueous solutions as these are most likely to occur as industrial liquid effluents.

III.1.1. Principles of Evaporation

The temperature at which water can be transformed into steam can be varied by changing the pressure above the solution. Thus deceasing the pressure below the 1 bar allows steam to be produced at <100ºC and by raising the pressure the temperature of transformation is raised above 100ºC.

The transformation of water into steam requires:

- the heat necessary to bring the water at its initial temperature to its boiling point at the defined pressure of the system,
- the heat required to transform the totality of this water into steam at the boiling point temperature.

III.2. TECHNOLOGIES OF IMPLEMENTATION

The heating a fluid requires an input of energy. Industrially, this energy is often of electrical in origin and constitutes a major source of expenditure. It is therefore essential to choose the type of evaporator to suit the nature and volume of waste stream to be treated. Indeed, as will be seen later, the amount of energy required can vary from 20 to 250 kWh/ton of waste to be treated!

Several types of evaporators exist on the market of which only one works at atmospheric pressure, these are:

- heat pump evaporators,
- mechanical steam compression evaporators,
- multiple effect evaporators,
- atmospheric evaporators.

III.2.1. Heat Pump Evaporators (Figure 2.1)

These evaporators, the treatment capacity of which is about to 200 L/h, use the principle of the heat pump. A gas (generally a Freon), compressed in a refrigerated compressor, is sent to the boiler under vacuum into which the liquid effluent is admitted. The gas transfers its energy to the effluent creating a spray and vaporising part of the water. The water vapour is then condensed on surfaces, cooled by the circulating gas, and the condensate is collected. The Freon gas from the boiler is cooled by passing through a heat exchanger before to entering the condenser and then being recompressed for recycle.

Heat pump evaporators are commonly used in small installations because of their ease of implementation and small dimensions. Their major drawback is the cost of operation:150-250 kWh/ton of evaporated waste or 10-17 € /t.

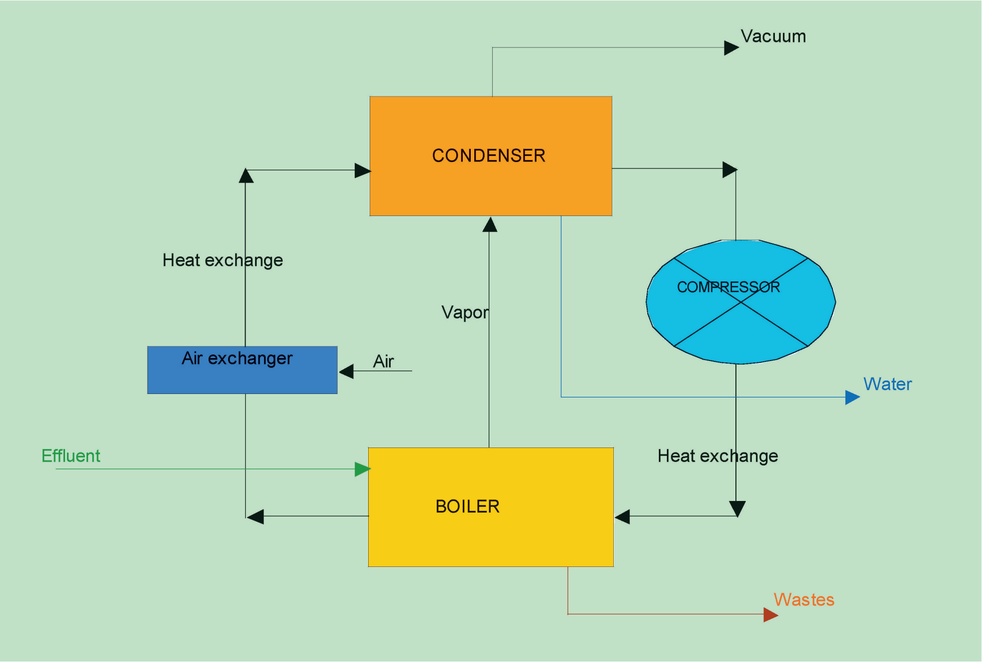


Figure 2.1. Heat pump evaporator

III.2.2. Mechanical Steam Compression Evaporator (Figure 2.2)

These evaporators are based on the use of the latent heat of spraying of the waste water as the source of energy.

The liquid effluent, continuously preheated by the hot water coming from the condensation process, is admitted into the evaporator where it is heated electrically. The steam created is compressed by an outside compressor and returned to the evaporator.

As soon as the process is started, the energy supplied to the compressor motor is sufficient to maintain the evaporation of the effluent without any additional energy contribution. Water is condensed and recovered at the evaporator exit and its contained heat is used to continuously preheat the incoming effluent to the evaporator.

Mechanical steam compression evaporators can be equipped with either centrifugal compressors or volumetric compressors. It is necessary to consider carefully of the type of compressor installed because it depends on the nature of the waste water to be treated. Indeed, the compression power and the increase of temperature, depends on the type of compressor: 4-5°C for centrifugal compressors; 15-20°C for volumetric compressors.

Evaporators using centrifugal compressors are reserved for lightly loaded waste water, with little tendency for furring and with little delay in reaching the boiling point.

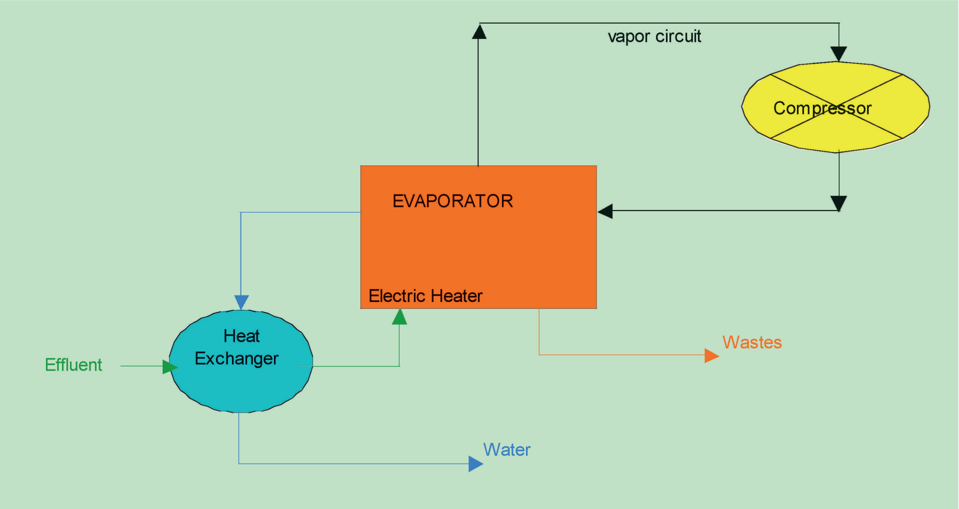


Figure 2.2. Mechanical steam compression evaporator

The relevant energy costs are:

- centrifugal compressor evaporators: 20-30 kWh/t of evaporated waste or 1.4-2 € /t,
- volumetric compressor evaporators: 60-90 kWh/t of evaporated waste or 4-6 € /t.

Mechanical steam compression evaporators, especially if equipped with a volumetric compressor, are reasonably versatile and less expensive in energy than the heat pump evaporators.

III.2.3. Multiple Effect Evaporators

Multiple effect evaporators (Figure 2.3) work with the exchange of heat from hot water or steam to treat the waste-water either in forced circulation (internal exchange), or by plate condensers (external exchange) mode. Spraying of the effluent can take place either over the boiler heater, or in an expansion room. The steam is condensed on cold water condensers working in closed circuit.

The advantage of this type of evaporator is the ability to multiply the number of treatment cells and hence decrease the energy cost proportionally. It is also very versatile and is not limited practically because number of cells can be adapted to the required evaporation capacity.

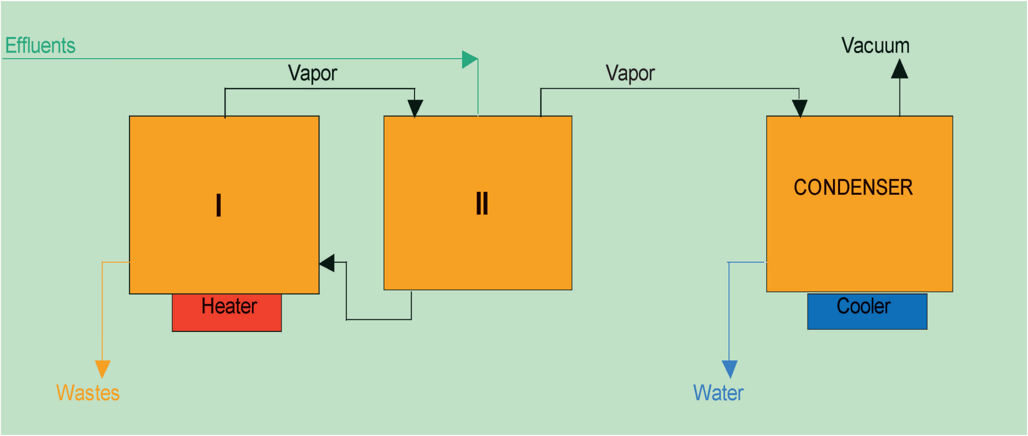


Figure 2.3. Multiple effect evaporator

The energy costs are:

- simple effect version: 700 kWh/t of evaporated waste water or about 16 €/t,
- double effect version: 9 €/t,
- triple effect version: 5 €/t.

III.2.4. Atmospheric Evaporators

In this type of evaporator, the effluent to be concentrated is heated at atmospheric pressure and its surface is constantly ventilated. The higher temperature of the waste water rises, the more rapidly the air in contact with the liquid is renewed, and the more the waste water is concentrated.

This technique has a very low investment cost but suffers major drawbacks with very high energy costs and atmospheric pollution requires the installation of a cleaning circuit.

II.3. ENCOUNTERED PROBLEMS

Whatever type of evaporator is chosen, two important phenomena can be met during use; crystallization due to the concentration of the waste water and corrosion due to the chemical aggressiveness of the concentrated waste water.

III.3.1. Crystallisation

Preliminary tests must be carried out on the waste water to be treated to determine the maximum concentration in the boiler before crystallisation occurs.

This concentration, called “factor of volumetric concentration”, is one of the important factors that determine the choice of the treatment process because the cost of the subsequent treatment of the concentrated wastes in Approved Treatment Centers is an important factor in the overall cost of exploitation.

III.3.2. Corrosion

The presence of some anions, notably chlorides and/or fluorides, constitutes a risk of corrosion of the boiler. So some precautions are required before admitting the effluent to the boiler notably that the level of the pH should not be < 4.5.

The treatment of waters containing chlorides and/or fluorides requires special quality of steel to be used in the construction of the boiler. Thus classical austenitic stainless steels are not suitable and on very high nickel content steels are preferred. Contrary to what is often stated, the titanium alloy, Ta6V, is not suitable because it quickly undergoes corrosion in such waste-waters.

Furring is another important phenomenon commonly met in operation. This furring of the surfaces of heat exchangers quickly results in a reduction of the quantity of the condensate. A simple wash of the relevant surfaces with sulfamic acid will clean the equipment. However great care must be taken if effluents containing cyanides are cleaned in this way!

III.4. INDUSTRIAL APPLICATIONS OF EVAPORATION*

Evaporation has proven to be a very efficient and reliable technology for treatment of industrial waste-water mainly due to its flexibility in the treatment of very different types of wastes, with a very high load of pollutants.

---

* These applications have been supplied by Cristina del Piccolo, LED Italia.

Evaporation is applied, for example in:

- the treatment of exhausted oil emulsion and die casting waste-waters producing a condensate that is re-used in the preparation of new emulsions. Thus for example, in Spain, Renault has installed a TC 30000 AA for the treatment of 1.5 ton/hour of oil emulsion,
- treating effluents from surface treatments, e.g. the plating industry (chrome plating, zinc plating etc), degreasing, tumbling waters, pickling solutions, regeneration eluates from resin demineralisation plants, etc.,
- the concentration of leachates and exhausted solutions from landfill and effluent disposal centres. A plant for the treatment of 200 ton/day of leachate has been constructed in a landfill near Athens in Greece that receives wastes from all around the city. Four hot water evaporators of the EW 40000 FF series have been installed: these use the free hot water stream from the co-generation plant (from the cooling of engines installed to produce electrical energy from biogas),
- the treatment of printing waste-waters containing ink, glue, etc., and waste-water from flexo printing etc. In Italy all the print works of the “La Repubblica” newspaper have installed Led Italia plants for the treatment of wash water from NAPP processes containing a photopolymer. Also in this application the distillate is re-used for the washing of NAPP processors, because water with no salinity is required (conductivity about 10 MicroS/cm is necessary),
- several different applications in the chemical and pharmaceutical industries for reactor wash waters etc.,
- power plants with zero liquid discharge (ZLD) for the treatment of reverse osmosis concentrate and resins eluates from demineralisation plants, or from desulfurisation processes. Led Italia (through Veolia Water Solutions and Technologies Italia) has combined with Alstom, a leading company in power plant construction and commissioning, in a ZLD plant with evaporation and crystallisation units for 3 ton/hour to be constructed in the South of Italy.

In most applications the condensate produced (treated stream) is recycled to the working process, thus achieving the status of Zero Liquid Discharge, this is becoming more appreciated by authorities thanks to the important recovery of water. If recycling is not possible as for instance in landfills, the condensate can be discharged.

In some cases it is also possible to reach the ZTD when the concentrate is recovered. An example is the electrolytic tinning for industrial packaging (mainly in food industry) where the tinning bath becomes diluted from carry over of water by the washed parts to be treated in the bath. Evaporation continuously removes water thus maintaining the concentration of the bath constant. The evaporated water can be used as wash water for prior treatments before tinning.

IV.

ION EXCHANGE

INDEX

IV.1. INTRODUCTION

Ion exchange is the reversible exchange of ions between a solid phase (*ion exchanger*) and a polar solution phase containing ions, the ion exchanger being insoluble in the medium in which exchange takes place. Thus if an ion exchanger R^-A^+, where R^- represents the solid matrix and A^+ exchangeable cations within the matrix, is placed in a solution containing B^+ cations, then an exchange reaction takes place according to equation 1a. Similarly exchange of anions can occur if the ion exchanger matrix carries positively charged ions, equation 1b.

$$R^-A^+ + B^+ \leftrightarrow R^-B^+ + A^+ \qquad 1a.$$

$$R^+X^- + Y^- \leftrightarrow R^+Y^- + X^- \qquad 1b.$$

Note that in the process of ion exchange there is an *exchange* of ions not a one-way uptake; the exchange is strictly *stoichiometric*; the exchange is *reversible*.

In general terms for multivalent ions these equations become:

$$z_B R^{z_A} A^{z_A} + z_A B^{z_B} \Leftrightarrow z_A R^{z_B} B^{z_B} + z_B A^{z_B}$$

$$z_Y R^{z_X} X^{z_X} + z_X Y^{z_Y} \Leftrightarrow z_X R^{z_Y} Y^{z_Y} + z_Y X^{z_X}$$

These are equilibria and thus equilibrium coefficients can be defined as:

$$K_A^B = \frac{[RB]^{z_A}[A]^{z_B}}{[RA]^{z_B}[B]^{z_B}} \qquad \text{and} \qquad K_X^Y = \frac{[RY]^{z_x}[X]^{z_y}}{[RX]^{z_y}[Y]^{z_x}}$$

These coefficients represent the *selectivity* of the ion exchanger for a particular ionic species and thus are generally termed the *separation factor* (α_A^B). These separation factors can be represented graphically as *ion exchange isotherms* (figure 1.1). If $\alpha_A^B > 1$ then exchange occurs and ion B is removed from solution, (Figure 1.1: isotherm 1) whereas if $\alpha_A^B < 1$ then exchange of B for A is unfavourable (isotherm 2) and if $\alpha_A^B = 1$ no exchange occurs (isotherm 4). Note that separation depends on concentration and on occasions a sigmoidal isotherm (3) is obtained where the separation factor changes from >1 to <1 as the total concentration in the system (*resin loading*) increases. Two other theoretical isotherms are possible, a horizontal isotherm 5, where $y = 1$, this is an irreversible isotherm because when $x > 0$ then $y = 1$. The second horizontal isotherm 6, where $y = 0$ indicates a situation where no exchange takes place with the resin.

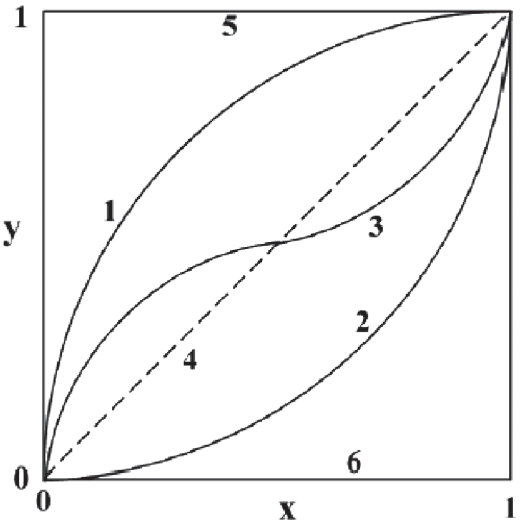
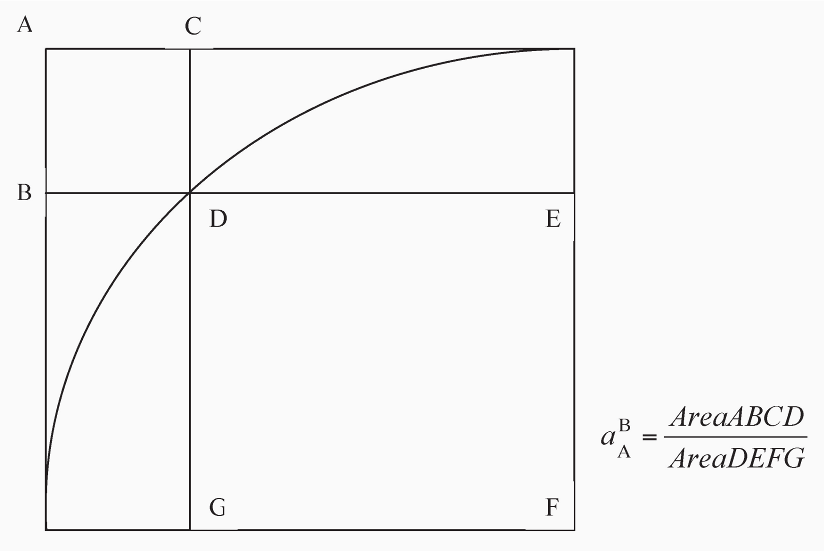


Figure 1.1. Typical ion exchange isotherms (where y = concentration fraction of B on resin phase and x = concentration fraction of B in solution)

The selectivity factors can be derived from these isotherms. Figure 1.2 shows the calculation of the selectivity factor for B over A at the given point D.



$$a_{A}^{B} = \frac{Area ABCD}{Area DEFG}$$

Figure 1.2. Calculation of selectivity factor α at point D

Examination of separation factors provides a general selectivity order for ions from dilute solution, thus multivalent ions are preferred over singly charged ions e.g. $M^{(Z+1)} > M^+$. More careful examination shows that selectivity among ions of the same charge depends on the nature of the matrix of the ion exchanger, see below. The capacity of an ion exchanger is measured in terms of milliequivalents/gramme, where the equivalent of an ion is the atomic mass of an ion divided by the numerical ionic charge.

IV.1.1. Types of Ion Exchanger

The phenomenon of ion exchange has been known for a long time with the mechanism of the process being established in the 1850s. The first examples of ion exchangers were found with clays and similar layered aluminosilicate structures. The search for alternative materials led to the use of sulfonated coals in the 1900s and the development of synthetic organic polymers in the 1930s. Currently the majority of commercial exchangers are based on styrene or acrylic polymers containing various functional groups substituted onto the polymer backbone to provide the ion exchange sites, copolymerised with divinylbenzene to promote crosslinking (Table 1.1). The nature of the functional group determines the primary exchange properties of the resin, i.e. cationic or anionic exchange, with the ion selectivity modified by the group acidity/basicity:

strong acid cation:

$Cs^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$; $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Cs^{2+}$;

weak acid cation:

$H^+ >> Cu^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Fe^{3+} > Ca^{2+} > Mg^{2+} > Na^+ > K^+ > Cs^+$;

strong base anion (Type 1):

$SO_4^{2-} > HSO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > HSiO_3^- > F^- > OH^-$;

weak base anion:

$OH^- >> SO_4^{2-} > HSO_4^- > I^- > NO_3^- > Br^- > Cl^- > F^-$.

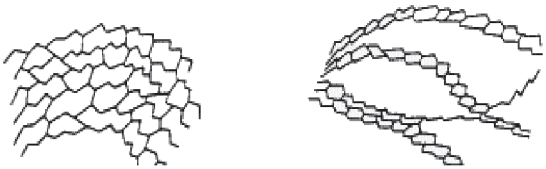
Resin Type	Matrix	Structure	Functional group	Approx. ionic capacity (meq g^{-1})
Strong acid	Styrene-DVB	gel macroporous	$-SO_3^-$	2.0 1.8
Weak acid	Acrylic-DVB	gel macroporous	$-COO^-$	4.2 3.0
Strong base (Type 1)	Styrene-DVB	gel macroporous	$-N(CH_3)_3^+$	1.3 1.15
Strong base (Type 2)	Styrene-DVB	gel macroporous	$-N(CH_3)(CH_2CH_2OH)^+$	1.3 1.15
Strong base (Type 1)	Acrylic-DVB	gel macroporous	$-N(CH_3)_3^+$	1.25 1.2
Weak base	Styrene-DVB	gel macroporous	$-N(CH_3)_2$	1.2 1.25
Weak base	Acrylic-DVB	gel macroporous	$-N(CH_3)_2$	1.6 1.0

Table 1.1. Common types of commercial polymeric resins

The overall polymeric structure of the matrix influences the mechanical strength, swelling characteristics, ion exchange equilibria and kinetics, and the choice here is between *gel*, *macroporous*, and *macronet* structures. The first commercial resins were gel type having a heterogeneous structure with some regions of high crosslinking and others where crosslinking is much less (figure 1.3.a) The non-uniform crosslinking and distribution of functional groups gives rise to regions within the bead with different characteristics and performance. Changing the synthetic process of polymerisation allowed the formation of a macroporous matrix with defined pore system between regions of high crosslinking that ensure the rigidity of the beads (figure 1.3.b). A typical average pore diameter in a macroporous resin is 150nm with a range between tens to several hundred nanometers, in contrast a gel resin has an apparent porosity of about 4nm typifying the average distance of separation of polymer chains. The usual resin cross-linking agent is divinylbenzene that inserts a spacer consisting of $-CH_2-C_6H_5-CH_2-$ groups between the polymeric chains. Using a smaller spacing group e.g. $-CH_2-$ produces a hypercrosslinked Macronet[1] resin that has some useful advantages.

---

[1] Macronet® resins are produced by Purolite.



a) gel b) macroporous

Figure 1.3. Types of resin structure

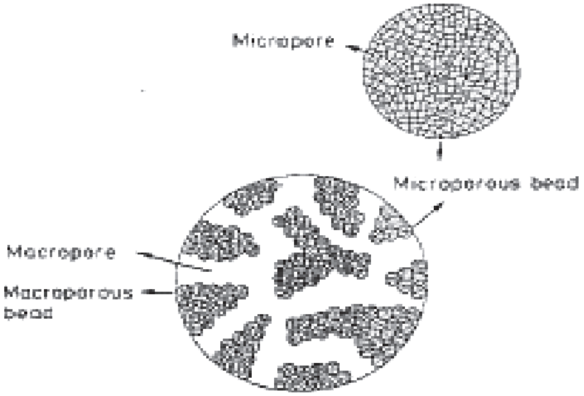


Figure 1.4. Presence of micro- and macro-pores in resin beads

In addition to the above strong and weak acid and base exchangers specialised resins are available substituted with chelating acid functional groups, e.g. aminophosphonate $-CH_2-NH(CH_2PO_3)^2$, imidodiacetate $–CH_2-N(CH_2COO^-)_2$, thiol –SH, thiocarbamide $–CH_2-SC(NH)NH_2$, etc. These resins have an enhanced selectivity for particular metal ions, e.g. transition metal ions, but their higher cost limits their application.

Inorganic matrices often based on layered structures have also been developed as ion exchangers. Examples include heteropolyacid salts; amphoteric oxides; inorganic phosphates; natural and synthetic zeolites. These have an advantage when treating strongly oxidising or radioactive solutions that may degrade the organic resins.

IV.1.2. Ion Exchange Processing

As described above ion exchange involves the interchange of ions within the solid exchanger structure with ions in the surrounding medium. This interchange occurs until the exchanger reaches ionic equilibrium as determined by the separation factor. Once this equilibrium has been reached no further exchange is possible and the exchanger has to be *regenerated* for further use. This cycle of loading and regeneration is an essential part of ion exchange operations.

Ion exchange operations are normally carried out in columns of resin with the feed solution containing the ‘polluting’[3] ions entering the top of the column. An even distribution of the feed over the column diameter is necessary to provide an even flow down the column (*down-flow operation*) and maximum use of the capacity of the resin. As the solution of polluting ions flows down the column chromatographic separation of the ions occurs according to their separation factors (figure 1.5) until the ions start to appear in the *eluant.* This is called *breakthrough* and breakthrough curves can be obtained (figure 1.6). Once the targeted pollutant reaches a certain concentration in the eluant (*breakthrough limit*) the column must be taken out of service and regenerated.

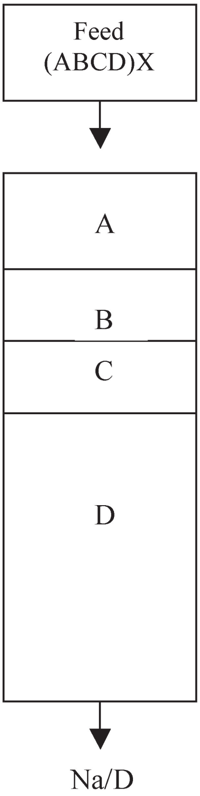


Figure 1.5. Chromatographic separation in an ion exchange column (sodium form)

---

[3] As this text is mainly concerned with effluent treatment for ease of description the term ‘polluting’ ions will be used in the text but ion exchange can also be used to concentrate, separate, and purify compounds.

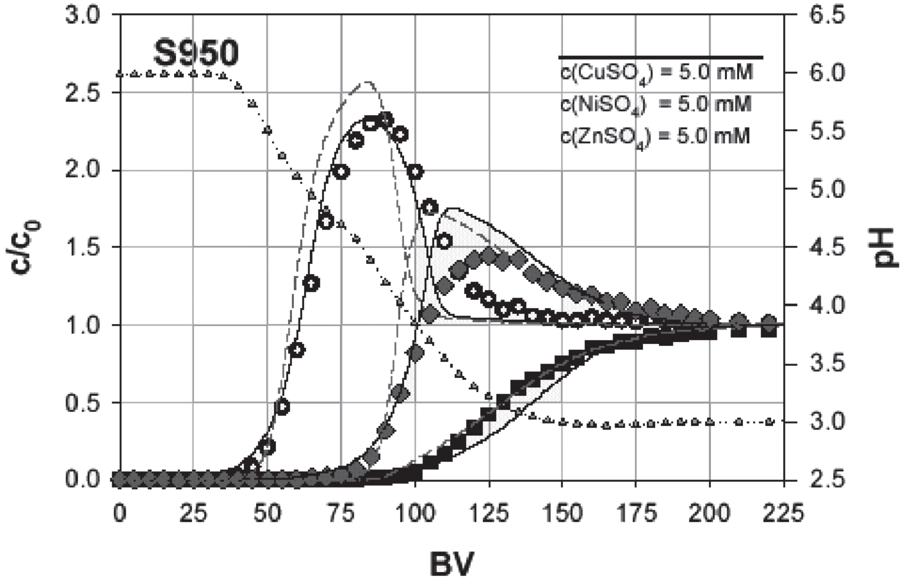


Figure 1.6. Breakthrough curve (Cu > Zn > Ni)

Regeneration is the reverse of the loading cycle and a concentrated solution of regenerant is use to remove the pollutant ions from the column. As the regenerant solution (X^-A^+) moves through the loaded resin the reverse exchange reaction occurs and the polluting ions are displaced (equation 2). Thus as the regenerant flows through the loaded resin the concentration of the regenerating species is reduced.

$$R^-B^+ + X^-A^+ \rightarrow R^-A^+ + X^-B^+ \ (X^-A^+) \qquad (2)$$

Two main flow regimes may be used in regeneration, *co-flow* where the flow of regenerant is the same as the loading cycle, usually down-flow, or *counter-flow* with the regenerant flow opposite to the down-flow loading cycle, entering the bottom of the column (*up-flow*).

Up-flow regeneration has a number of advantages:

1. The upward movement of the solution will tend to displace any particulate matter trapped in between the resin beads and allow them to be removed.
2. In down-flow operation ions with the highest selectivity factor, ('A' ions in figure 1.5) concentrate at the top of the column. In the case of *co-flow regeneration* such ions will have to traverse the whole of the column and regeneration in the lower regions will be less efficient with the resin containing a significant fraction of polluting ions. This will lead to *leakage* of these pollutant ions at the start of the loading cycle (figure 1.5).
3. The overall regeneration efficiency is higher and thus the resin bed is used more effectively and a lower resin inventory is required.

To maintain the advantages of counter-flow operation it is essential that the resin bed remains consolidated and undisturbed during operation and recycle to ensure that the fully regenerated resin at the base of the column is not mixed with resin with poorer regeneration from the top. Thus back-washing of a column in counter-flow operation is not usual, if it is necessary to backwash then more regenerant is required to ensure adequate regeneration.

As a concentrated regenerant solution is used the volume of spent regenerant containing the pollutants is smaller than the feed solution thus allowing easier disposal or recovery.

Following regeneration the resin is rinsed free of regenerant before returning to the loading cycle.

IV.2. ION EXCHANGE EQUIPMENT

The equipment required for ion exchange processing is basically very simple consisting of a cylindrical column which can be made of almost any inert material e.g. plastic, glass, metal, fitted with values to allow access for the feed and eluant solutions at the top and bottom. The inside of the column is fitted with some type of screen at the base to retain the resin beads and a carefully designed liquid distributor at the top to ensure equal flow of the feed solution across the resin bed. As the resin beads swell and contract as the exchange process takes place care has to be taken to ensure adequate free capacity inside the column. Such equipment is termed *fixed column configuration* and is usually adequate for effluent treatment. In this configuration the resin is loaded until breakthrough and then the column is removed from service and regenerated thus it is operated as a *batch process*. An approximation to continuous operation can be devised by operating several fixed columns in series and switching between columns as appropriate. True continuous operation is possible and is used commercially, for example in the recovery of uranium from leach solutions, but as such operations are more difficult and require specialised equipment it is unlikely that they would be used in effluent treatment so will not be described here.

IV.3. LIQUID ION EXCHANGERS

Liquid organic compounds that contain acidic or basic functional groups can also function as ion exchangers. These are extensively used in hydrometallurgy for the recovery of metallic species from aqueous solutions using liquid-liquid extraction (solvent extraction). These extractants have much greater selectivity than solid resin ion exchangers and have been used in the past in closed circuit operations to recover metal values from liquid effluents. However the use of volatile organic compounds as carriers for the extractant means that such operations are not now considered environmentally friendly. Current developments in the use of non-volatile ionic liquids as carriers may allow the use of these organic extractants for effluent treatment in the future if the cost of the ionic liquids can be reduced.

Adsorption of liquid ion exchangers into a organic polymer matrix, i.e. impregnated resins, or layered inorganic clays, allows the selectivity of the extractants to be used in the treatment of liquid effluents without the problems of a volatile organic solvent. These materials can be used in a similar way to resin ion exchangers; however they do have a finite life-time as the exchanger liquid will leak from the matrix. This does potentially cause an environmental hazard but this can easily be reduced by the use of an inert adsorbent such as active carbon to remove the organic compounds from the column eluant.

IV.4. BAT ASSESSMENT OF THE USE OF ION EXCHANGE FOR THE TREATMENT OF EFFLUENTS

(BREF 07 – Mining and Metallurgical Industries – Section 2.9.2.2.6):

Advantages

- relatively inexpensive,
- range of commercial products available from several manufacturers,
- well established and tested procedures,
- clean-up to ppb levels (selective resins to ppt levels),
- easy to use with other techniques - e.g. precipitation in an integrated waste-water treatment,
- can be selective for heavy metals with suitable resins,
- can be applied to different flow regimes: continuous, batch, intermittent and relatively large volumes.

Disadvantages

- cannot handle high concentrations of metals (*true - main advantage as polisher following other treatment e.g. precipitation)*,
- beads easily fouled by particulates and some organic compounds *(well recognised problem but minimised by backwashing and choice of resin)*,
- normal resins not selective *(true)*,
- spent resin often necessary to treat as toxic waste *(resin generally used for many cycles - however for final disposal can be incinerated)*,
- matrix degrades with time and with certain waste materials - radioactive; strong oxidants *(when treating such solutions inorganic exchangers can be used - more resistant)*,
- performance sensitive to pH of effluent *(true)*,
- large volumes require large columns *(true),*
- selective ion exchangers expensive and currently have limited commercial use *(true),*
- column flow-rates rather slow and hence cycle times can be lengthy *(true),*
- regeneration time-consuming and spent regenerant may require treatment as toxic waste *(regeneration provides concentrated solution of removed metals that may be recycled or recovered by other methods, electrolysis or precipitation, hence reducing toxicity).*

General References on Ion Exchange

F G Helfferich, Ion Exchangers, McGraw-Hill Book Company, Inc. 1962.

A Clearfield, Inorganic Ion Exchange Materials, CRC Press, Inc. Boca Raton, Fla 1982.

K Dorfner (ed), Ion Exchangers, Walter de Gruyter, Berlin, New York, 1991

M J Slater, The Principles of Ion Exchange Technology, Butterworth-Heinemann Ltd., Oxford, 1991

C E Harland, Ion Exchange: Theory and Practice, The Royal Society of Chemistry,

Letchworth, Herts, U.K. 1994.

J Marinsky, Y Marcus, Ion Exchange and Solvent Extraction – A series of advances Volumes 1-14, Marcel Dekker New York 1980-2000.

General References on Liquid/Liquid (Solvent) Extraction

T C Lo, M H I Baird and C Hanson (eds), Handbook of Solvent Extraction, Wiley-Interscience, New York, 1983

J D Thornton (ed), Science and Practice of Liquid-Liquid Extraction, Oxford University Press, 2 volumes, 1992

J C Godfrey and M J Slater (eds), Liquid-liquid Extraction Equipment, John Wiley and Sons, Chichester, UK 1994

J Rydberg, M Cox, C Musikas and G Choppin (eds), Solvent Extraction: Principles and Practice, 2nd Edition, Marcel Dekker, New York 2004

V.

MEMBRANE PROCESSES

INDEX

V.1. INTRODUCTION

During the three last decades, membrane separation processes have evolved from a simple laboratory technique to utilization in important operations with significant technical and commercial impact. Nowadays, membrane technology is an established part of several industrial processes. Membrane and module sales in 1998 were estimated at more than US$ 4.4 billion worldwide[1] shared among different applications. If equipment and total membrane systems are also considered, the estimation would be double this figure.

The industrial development of membranes dates back to the 1960s with the implementation of the first water desalination plants based on reverse osmosis technology. Meanwhile, haemodialysis membranes arose as a major advance in solving problems of kidney deficiency. Since this pioneering period in which European industries played a prominent role, membrane processes have evolved and found use in many other applications with a strong socio-economic impact on citizens' daily life (Figure 1.1).

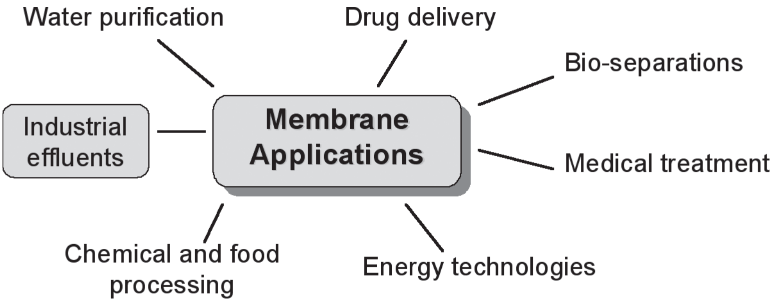


Figure 1.1. Membrane technology applications in citizens' daily life.

V.2. MEMBRANES AND MEMBRANE PROCESSES

A membrane is a permeable or semi-permeable solid phase, e.g. polymer, inorganic or metal, which restricts the motion of certain species. It controls the relative rates of transport of various species (solvent, solutes or ions) through itself thus giving one product depleted in certain components and a second product concentrated in these components. The membrane is inserted in a module as depicted in Figure 2.1 (example of a pressure-driven process). Its performance is defined in terms of two factors, flux and selectivity.

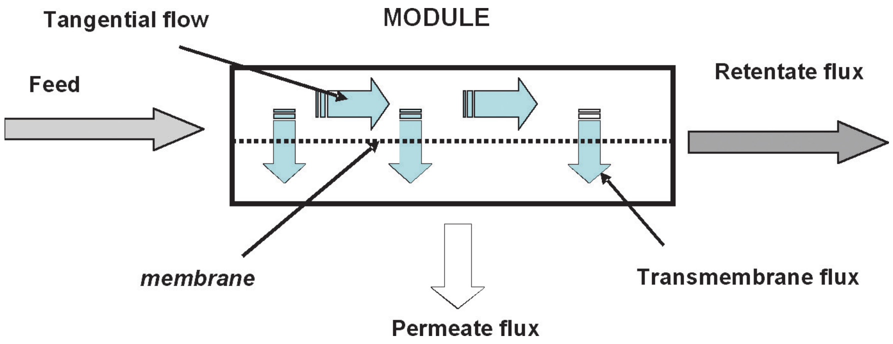


Figure 2.1. Schematic drawing of a separation process

Flux (or permeation rate) J is the volumetric or mass flow rate of fluid passing through the membrane per unit area of membrane and unit of time expressed by:

$$J = \frac{\Delta P}{\mu . R_m}$$

where ΔP is the trans-membrane pressure, μ is the viscosity of the crossing solution (permeate), R_m is the hydraulic resistance of the membrane, and the hydraulic permeability, L_p is defined as:

$$L_p = \frac{1}{\mu . R}.$$

Retention is the fraction of solute in the feed retained by the membrane. It is expressed by the relationship:

$$R = 1 - \frac{C_p}{C_f}$$

where C_p and C_f are the solute concentrations in the permeate and feed respectively.

Selectivity is a measurement of the relative permeation rates of different components through the membrane.

Membrane manufacturers use the concept of “cut-off” to characterize their membranes. The Molecular Weight Cut-Off (MWCO) being defined as that molecular weight which is 90% rejected by the membrane.

In the chemical process industry one often encounters the problem of separating a mixture and its components. Membranes can in principle carry out most of the separation processes and can complement or provide an alternative for chemical processes like distillation, extraction, fractionation, adsorption, etc. Some advantages of membrane filtration are: a low energy consumption, continuous separation, relatively simple scale-up, and versatility for almost any kind of separation.

Membranes may be classified according the driving force at the origin of the transport process: (i): a pressure differential leads to micro-, ultra-, nano-filtration and reverse osmosis; (ii): a difference of concentration across the membrane leads to diffusion of a species between two solutions (dialysis); (iii): a potential field applied to an ion exchange membrane leads to migration of ions through the membrane (electrodialysis, electro-electrodialysis (Figure 2.2) and electrochemical devices), (Tables 2.1 and 2.2, Figure 2.3).

Separation mechanism	Membrane separation process
Size exclusion (filtration)	nanofiltration (NF), ultrafiltration (UF), microfiltration (MF)
Solubility/diffusivity	reverse osmosis (RO), gas separation (GS), pervaporation (PV), liquid/liquid membranes (LM)
Charge	electrodialysis (conventional and bipolar)

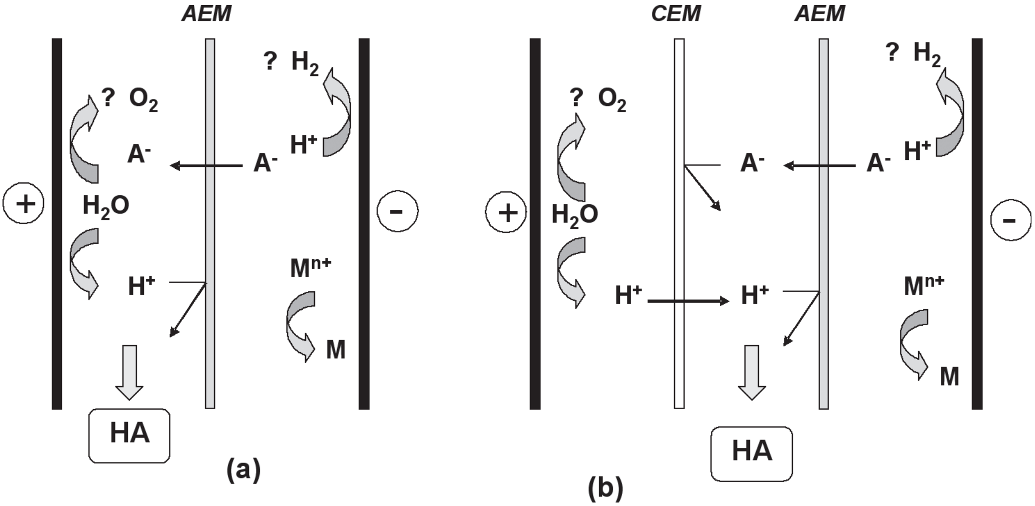
Table 2.1. Membrane separation defined according to the mechanism of separation

Membrane process	Pore size	Membrane type	Driving force	Main applications
Microfiltration MF	50 nm-5 µm	Symmetric and asymmetric microporous	Hydrostatic pressure 0.5-5 bars	Clarification, sterile filtration
Ultrafiltration UF	5-100 nm	Asymmetric microporous	Hydrostatic pressure 1-9 bars	Separation of macromolecular solutions
Nanofiltration (NF)	1-5 nm	Asymmetric	Hydrostatic pressure 4-20 bars	Separation of small organic compounds and multivalent ions
Reverse Osmosis (RO)	dense	Asymmetric, composite with homogeneous layer	Hydrostatic pressure > 20 bars	Production of "pure" water
Dialysis (D)	dense	Symmetric microporous	Concentration gradient	Separation of micro-solutes and salts from macromolecular solutions
Membrane distillation (MD)	10-100 nm	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis (ED)	dense	Charged membrane	Electric field	Separation of ions from water and non-ionic solutes

Table 2.2. Main solid/liquid and liquid/liquid membrane separation process

Membrane process	Pore size	Membrane type	Driving force	Main applications
Electro-electrodialysis (EED)	dense	Charged membrane	Electrical field	Separation of ions from water and ionic solutes
Liquid membranes (LM)	10-100 nm	Microporous, liquid carrier	Concentration, reaction	Separation of ions and solutes from aqueous solutions

Table 2.2. Main solid/liquid and liquid/liquid membrane separation process



(a): A is a non-oxidative anion; AEM anion-exchange membrane
(b): A is an oxidative anion. AEM and CEM: anion- and cation-exchange membranes

Figure 2.2. Examples of an electrical-driven membrane process: Electro-electrodialysis for the recovery of a mineral acid HA from an acid-salt effluent.

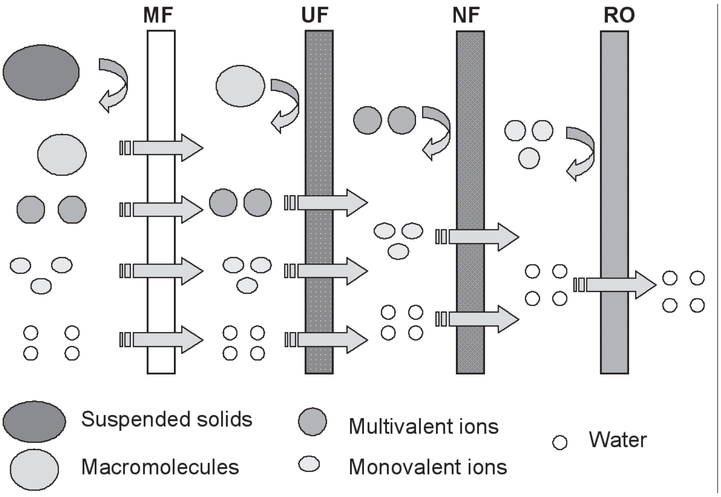


Figure 2.3. Species separation during pressure-driven membrane process (normal or perpendicular flow conditions)

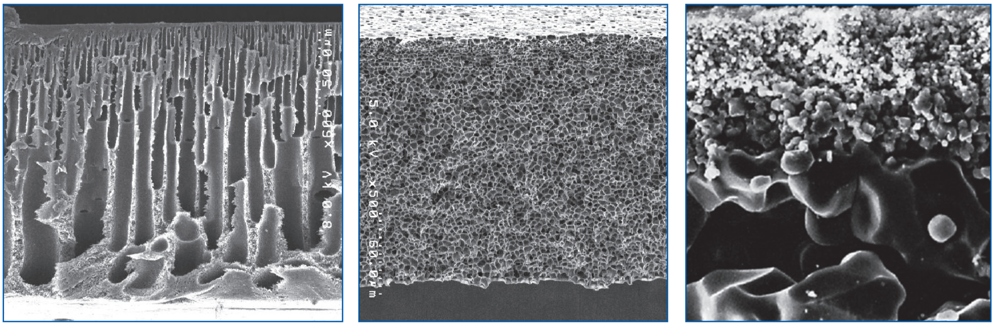
V.2.1. Choice of Membrane

For pressure-driven membrane processes, the choice of membrane is determined by the specific application, for example: particulate or TOC removal, hardness reduction, or potable or ultra-pure water production. The most widely used membranes for RO are cellulosic (CA) and polyamide (PA) types rated at 97-99% NaCl rejection. Nano-filtration also uses CA or PA membranes, with characteristic salt rejections from 95% for divalent salts to 40% for monovalent ions and an approximate 300 molecular weight cut-off (MWCO) for organics. The most common UF membranes are polysulfone (PS) having a 1000-100,000 MWCO (Table 2.4). Typical physical properties of membrane materials are given in Table 2.3.

Properties	Mineral membranes	Organic membranes
Membrane process	MF, UF, NF	MF, UF, NF, RO
Thermal resistance	> 400 °C	> 150 °C
Chemical resistance (pH)	0 to 14	2 to 12
Mechanical resistance	Good	Less good
Oxidant tolerance	Good	Depends on polymer
Compaction	Very good	Sensitive
Duration life	10 years	3-5 years

Table 2.3. Which type of membrane for which process?

Examples of the different types of membrane structure are depicted in Figure 2.4.



Polymer: asymmetric | Polymer: homogeneous | Ceramic: asymmetric

Figure 2.4. SEM of polymer and ceramic membranes for pressure-driven membrane processes

For electrical-driven membrane processes, the choice of the membrane depends on the nature and the composition of the effluent to be treated. For example, the treatment of acid effluents requires anion-exchange membranes (AEM) with a low proton leakage (Figure 2.5.a), that of effluents containing both monovalent and divalent cations require modified cation-exchange membranes (mCEM, Figure 2.5.b).

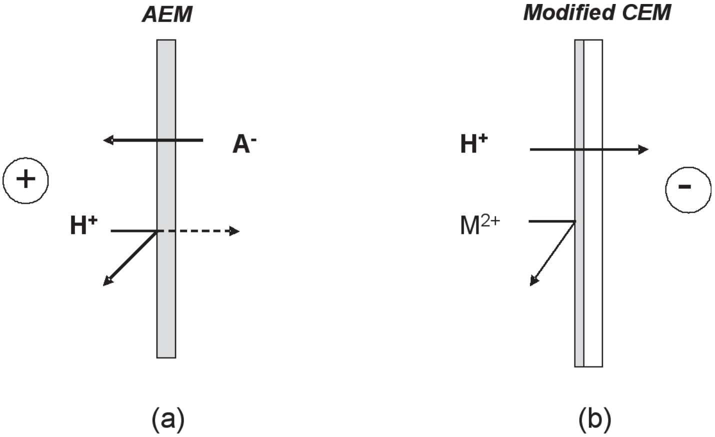


Figure 2.5. Specific ion-exchange membranes for the treatment of liquid acid effluents

For example, modified CEM and AEM are used for the recovery of acid from acid effluents containing metallic divalent salts as depicted in Figure 2.6.

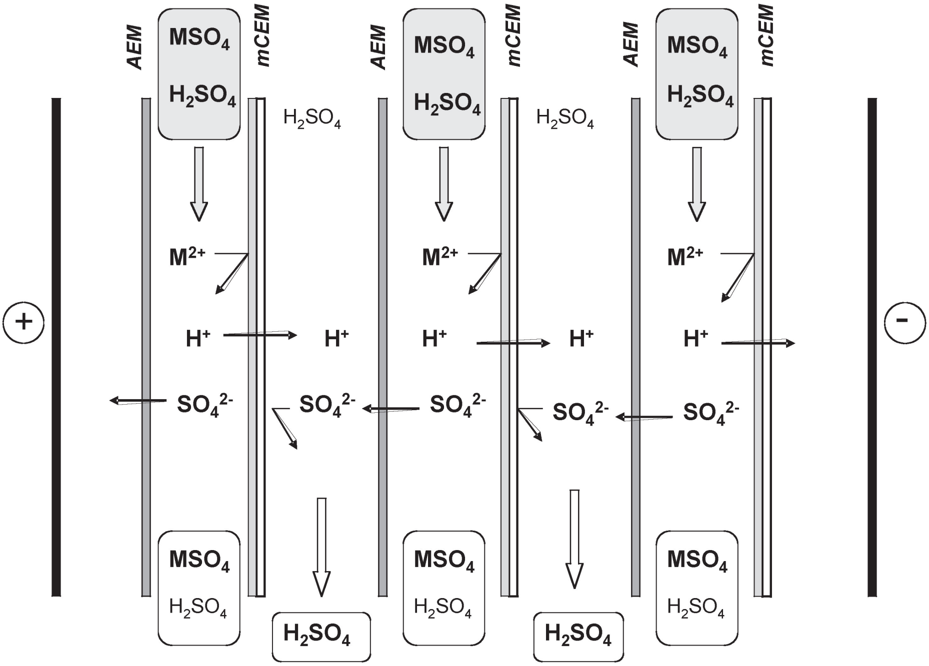


Figure 2.6. Example of ED for the recovery of acid from zinc hydrometallurgy.
(M is mainly Zn, but also includes Mg and Mn)

Ion-exchange membranes can operate at temperature up to 70-80°C. Their life duration (1-3 years) depends on their chemical behaviour versus oxidative media or extreme pH conditions.

V.2.2. Choice of membrane process

Cross-flow (tangential flow) membrane filtration (Figure 2.1) is generally considered to be the most efficient configuration as it reduces membrane fouling and provides a more consistent flux (Figure 2.6). Typical process conditions and applications of four pressure-driven membrane processes as depicted in Figure 2.3 (perpendicular flow conditions for a better comprehension) and reported in Table 2.4 (classic cross-flow).

Process	Component retained	Transmembrane pressure	Process applications
RO	99% of most ions, most organics over 150 MW	15-70 bars	Brackish sea water, desalting, boiler feed purification, pre-treatment to ion exchange, ultra-pure water production
NF	95% of divalent ions, 40% of monovalent ions, organics greater than 200-300 MW	9-20 bars	Hardness removal, organic and microbiological removal, dye desalting, colour removal
UF	Most organics over 1000 MW	2-9 bars	Pre- and post-treatment to IX, beverage clarification, concentration of industrial organics and dilute suspended oils, removal of pyrogens, bacteria, viruses, and colloids
MF	Small suspended particles greater than 0.1 mm	1.5-4 bars	High volume removal of small suspended solids.

Table 2.4. Cross-flow membrane processes

V.2.3. Choice of Module Design

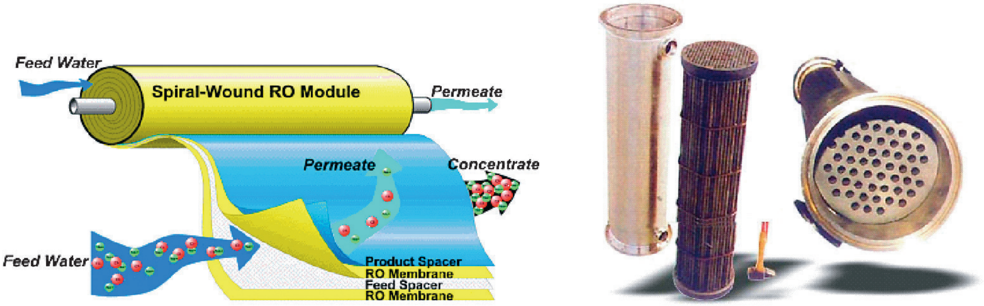
There are four major configurations for membrane modules: plate and frame units, hollow fibre, tubular and spiral-wound (Table 2.5).

The choice of the module is mainly determined by economic considerations. This does not mean that the cheapest configuration is always the best choice because the type of application is also very important. In fact the functionality of a module is determined by the type of application. Although the costs of the various modules may be appreciable, each of them has its field of application. Despite being the most expensive configuration, the tubular module is well suited for applications with a high fouling tendency because of its good process control and ease of membrane cleaning. In contrast, hollow fibre modules are very susceptible to fouling and are difficult to clean. In this case, pre-treatment of the feed stream is therefore important.

	Cost	Packing density	Operating pressure capacity	Membrane types	Fouling resistance	Cleanability
Spiral wound	Low	High	High	Many	Fair	Fair
Hollow fibre	Low	UF high RO v high	UF low RO high	Few	UF good RO poor	UF good, RO poor
Tubular	High	Low	UF moderate	Few	Very good	Very good
Plate & frame	High	Moderate	High	Many	Fair	Fair

Table 2.5. Comparison of cross-flow membrane configurations

Often it is possible to choose between two or more different types which are competitive with each other, for example hollow fibre and spiral wound modules for seawater desalination and pervaporation. In diary applications or in the pulp and paper industries, tubular or plate-and-frame modules are used. In electro-membrane processes (electrodialysis and electro-electrodialysis), the plate-and-frame module is recommended (Figures 2.7 and 2.8).



Spiral-wound RO module

Multi-channel tubular module

Figure 2.7. Spiral wound and tubular modules

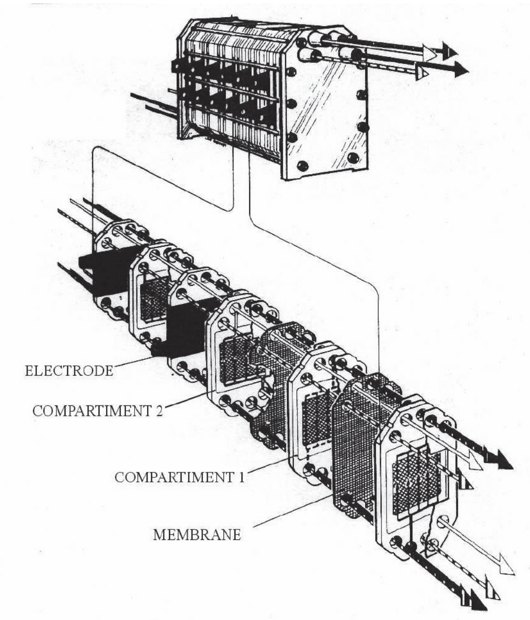


Figure 2.8. Plate-and-frame module (for electrodialysis or electro-electrodialysis)

V.2.4. Choice of System Design

The design of membrane filtration systems can differ significantly because of the large number of applications and module configurations. The module is the central part of a membrane installation and is often referred to as the separation unit. A number of modules (separation units) connected together in series or in parallel is called a stage. For industrial applications, a cross-flow operation is preferred because of the low fouling tendency due to reduced concentration polarisation. (Figure 2.9)

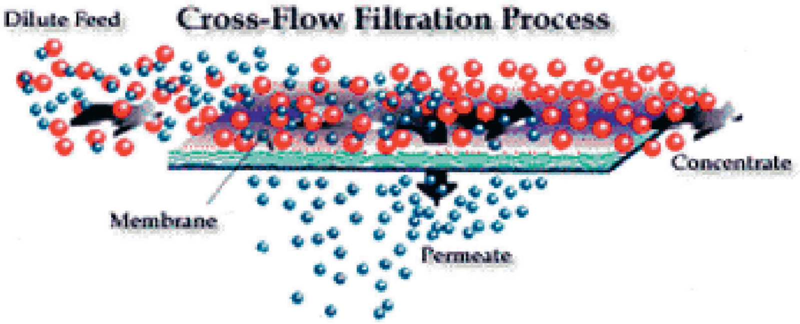
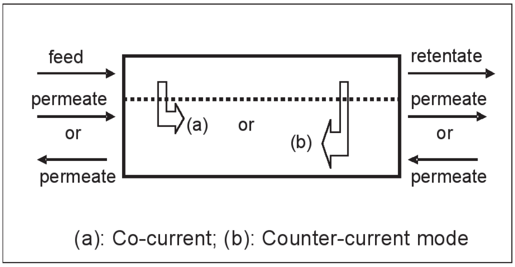
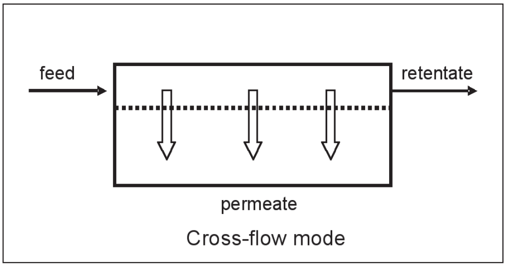
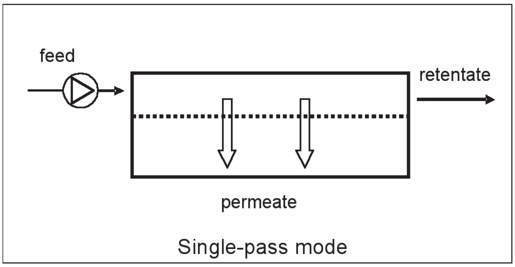


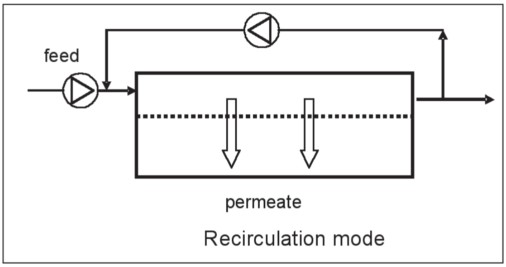
Figure 2.9. cross-flow filtration process

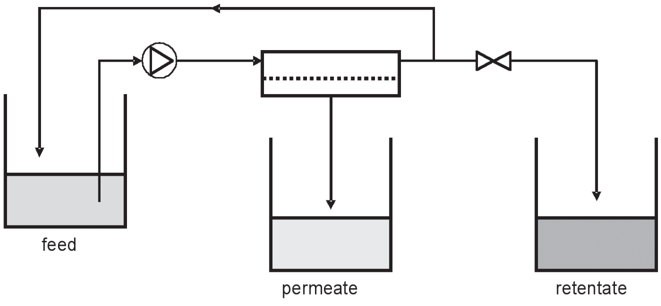
Various cross-flow operations can be distinguished co-current, counter-current, single pass, recirculation system, batch system, cascade systems, as depicted in Figure 2.10.[3]











Batch system mode

Figure 2.10. Some examples of cross-flow operation modes

For electrical-driven membrane processes (ED or EED), there are several operating modes. Depending on the feed solution composition and the product requirements, ED or EED units may be operated in a batch-type, in a continuous, or in a feed-and-bleed mode with partial recycle of the diluate and the concentrate streams.[1]

V.3. LIMITING PHENOMENA

Due to the selective character of membranes, limiting phenomena occur at the solution membrane interface. They can be gathered according to concentration polarisation. Membrane separations which are severely affected by concentration polarisation are ultra-filtration and electrodialysis.

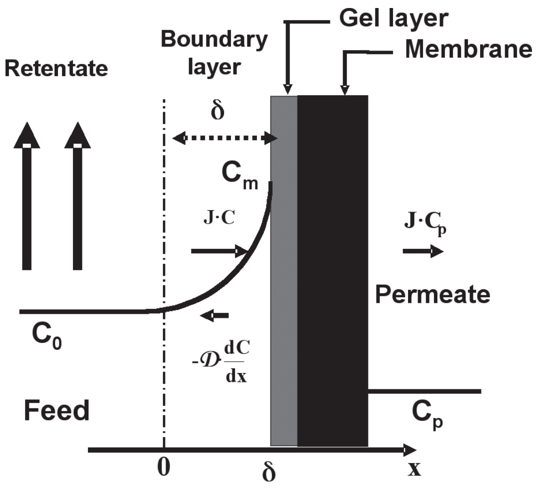


Figure 3.1. Concentration polarisation during a pressure-driven membrane process

Membrane fouling is a major cause of the reduction in flux during pressure-driven membrane processes, particularly in UF and MF, when feed pre-treatment is not used. Fouling consists in the deposition of retained particles (colloids, salts, macromolecules, etc.) onto the membrane surface or within the membrane pores (Figure 3.1). The build up of this deposit (gel layer) causes a continuous decline in flux with time.[4]

The balance sheet of the matter transfer can be written as:

$$J.C - D.\frac{dC}{dx} = J.C_p \qquad \text{leading to:} \qquad J = \frac{D}{\delta} Ln\left(\frac{C_m - C_p}{C_0 - C_p}\right).$$

Thus to increase the flux, the thickness of the boundary layer must be decreased. Improved hydrodynamic conditions, regular membrane cleaning, or application of reverse pressure for a short period to allow the flux to recover.

Electrodialysis is also subject to flux reduction by concentration polarisation (Figure 3.2). Here concentration polarisation is due to the difference in transport numbers of the counterion between the membrane and the solution. Gradients of concentration arise in the diffusion layers (Figure 3.2) and when the concentration of the counterions becomes negligible at the solution-membrane interface, a limiting current appears.

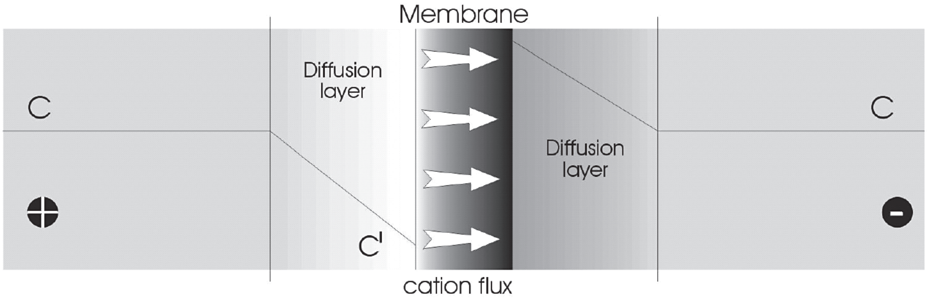


Figure 3.2. Concentration polarisation during electrodialysis

The limiting current density is given by: $J_{\lim} = \frac{z.D.F.C}{(t_m - t_s)}$, t_m and t_s being the transport numbers of the counter-ion in the membrane and in the solution, respectively (Figure 3.3).

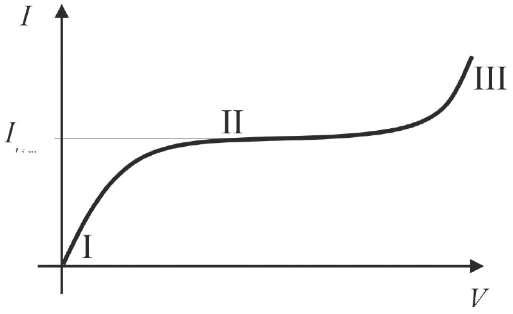


Figure 3.3. Limiting current during electrodialysis

If the current density is allowed to exceed j_{lim}, then the current crossing the membrane must be carried by another ion and dissociation of water occurs at higher current density. The limitations of the rate of ion transport through a membrane can be seen from a current density versus voltage plot for the membrane as depicted in Figure 3.3. This current-voltage plot is composed of three regions: I, an ohmic region in which current is carried by the ions of the electrolyte, II a plateau-shaped region corresponding to the limiting current, and region III in which the water splitting occurs. Because D/Δ is equal to k the mass transfer coefficient, j_{lim} is strongly determined by the hydrodynamics of the system (i.e. cross-flow velocity, geometry of the cell). Moreover, the distance between membranes has to be very small to reduce the ohmic drop due to the electrolyte thickness. In practice, separators of 0.8-1.5 mm thick acting as turbulent promoters are introduced alternately with the membranes.

V.4. MEMBRANE TECHNOLOGIES FOR POLLUTION CONTROL OF LIQUID STREAMS

In the treatment of liquid effluents, primarily waste-waters, the type of pollutant or pollutants has a strong influence on the selection of treatment technologies.[2] Some classes of pollutants which can be present in water are given in Table 4.1.

Species	Examples
particles, suspended solids, micro-organisms	oil in emulsions, settable solids, suspended solids, large solids, fibres and waste materials, fine particles
inorganics (dissolved)	heavy metals (Cd, Hg, Pb, Cr), salts (ammonia, nitrate, cyanide, etc.), nuclear wastes (Cs^{137}, Sr^{90}), acids, alkalis
volatile organics	aromatics (benzene, toluene, xylene), aliphatics (hexane, heptane), alcohols (methanol, ethanol), ketones (acetone, methyl or ethyl ketone), halogenated hydrocarbons (chloroform, ethylene chloride)
non-volatile organics	phenolic, polyaromatic compounds, micro-solutes (pesticides), surfactants, dyes

Table 4.1. Pollutants generally present in waste-waters

Membrane technologies for pollution control of liquid streams are shown in Table 4.2.

	Suspended colloidal and solids removal	Dissolved organic removal	Dissolved inorganic removal	Micro-organism removal
Electroelectro-dialysis			x	
Electrodialysis			x	
Microfiltration	x			x
Ultrafiltration	x	x		x
Nanofiltration	x	x	x	x
Reverse osmosis	x	x	x	x

Table 4.2. Principal membrane technologies for pollution control

Finally, in Table 4.3 the main applications of membrane technologies in the pulp and paper industry are collected.

Separation	Application
UF of Kraft	Effluent from the first stage of caustic extraction during pulp bleaching
UF of process effluent spent sulfite liquors	Digested liquors from spent sulfite chemical pulping. Recovery of lignosulfonates and sugars.
UF of Kraft black liquor	Recovery of alkali lignins
RO of sulfite liquors	Concentration of spent sulfite liquors
RO of paper machine effluents	Recycling of water
RO of wash waters	Preconcentration of sulfite contaminated wash water before evaporation.

Table 4.3. Membrane processes in the pulp & paper industry

References

1. Strathmann H., Membrane processes for sustainable industrial growth, *Membrane Technology*, **113**, 9-11 (1999).
2. Scott K., Handbook of Industrial Membranes, First Edition, Elsevier Advanced Technology (1995).
3. Marcel Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers (1991).
4. Richard W. Baker, Membrane Technology and Applications, Second Edition, Wiley (2004).

General References

- C. Mack, J. E. Burgess and J. R. Duncan, *Membrane Bioreactors for Metal Recovery from Waste-water: A Review,* Water SA, **30**(4), 521-532 (2004).
- B. Van der Bruggen, C. Vandecasteele, T. Van Gestel, et al., *A Review of Pressure-Driven Membrane Processes in Waste-water Treatment and Drinking Water Production,* Envir. Progr. **22**(1), 46-56 (2003).