Final Report

NATO/CCMS Pilot Study on Clean Products and Processes

2006 Annual Meeting
Kalyon Hotel, Istanbul, Turkey
May 7-12, 2006

Topical Symposium, 10th of May, 2006
Water Reuse and Recycling

Hosted by:

Middle East Technical University (METU), Ankara, Turkey

Sponsored by:

TÜBİTAK

MRC

FORD OTOSAN

KOCAELİ CHAMBER OF INDUSTRY

GOODYEAR

Preface

This is the final report for the Ninth Annual Meeting of the NATO/CCMS Pilot Study on **"Clean Products and Processes"** which is co-sponsored by NATO/CCMS Program and the U.S. Environmental Protection Agency (EPA). The meeting was held in Istanbul, Turkey on 7-12 May 2006. The host of the meeting was Professor Aysel T Atimtay from the Department of Environmental Engineering of Middle East Technical University (METU) located in Ankara, Turkey.

The purpose of the annual meetings was to bring scientists and researchers working on cleaner production from different countries together, and form a platform for exchange of ideas, knowledge and experiences. The ultimate goal was to increase collaboration between the researchers, to develop joint and innovative research projects and programs, thus, finding solutions to environmental problems.

One day during this meeting was allocated for a Special Topical Symposium which was on May 10, 2006. This year's topic was chosen as **"Water Reuse and Recycling"** which is becoming more and more important every year, especially in the Mediterranean region. Eleven papers were presented in this symposium by specially invited speakers who are well known in this field. Furthermore, the program of the meeting included one-day technical excursion to a research laboratory where several research projects on clean products and processes are conducted. Additionally, a tire manufacturing company and an automotive industry were visited to see the applications of clean production, environmental management and sustainable practices.

In this final report there are abstracts and presentations of thirty five papers out of which eleven of them belonged to the Topical Symposium. 32 delegates from 22 countries participated in the meeting and made presentations. There was also an open discussion held during this meeting on "Metrics for Sustainable Technologies" moderated by the Director of the Pilot Study, Dr. Subhas Sikdar.

We would like to extend our thanks to the sponsors for the meeting; U.S. EPA, Middle East Technical University, TUBITAK- Marmara Research Center, Kocaeli Chamber of Industry, Goodyear Tire Manufacturing Company and Ford Automotive Company for welcoming the delegates to a guided tour in the companies and/or research laboratories, and supporting us in every way for this meeting to be successful.

Istanbul, Turkey, 7 July 2006

Professor Aysel T. Atimtay, Middle East Technical University (METU), Ankara, Turkey

Dr. Subhas K. Sikdar, Pilot Study Director, Environmental Protection Agency, U.S.A.

Daniel J. Murray, Jr., Pilot Study Co-Director, Environmental Protection Agency, U.S.A.

METU U.S. EPA

NATO/CCMS Pilot Study on Clean Products and Processes
2006 Annual Meeting
Kalyon Hotel, Istanbul, Turkey
May 7-12, 2006

Final Program

Sunday, May 7, 2006

18:00 Reception at hotel

Monday, May 8, 2006

09:00 Welcome and Opening Speeches
09:15 Welcome to Turkey, **Vice Rector of METU, Prof. Dr. Fatoş Y. Vural**
09:30 Welcome to Istanbul, **Mayor of Istanbul**
09:45 Welcome by the Governor of Istanbul (**Deputy Governor Mr. Gazi Kaya)**
10:00 **Dr. Subhas Sikdar,** Pilot Study Director, U.S. Environmental Protection Agency, (USA)
Professor Aysel T. Atimtay, Host of the Meeting, Middle East Technical University (Turkey)

10:30 Introduction of Country Delegates and Participants

11:00 Overview of the Meeting Agenda, Technical Program and Tours
Mr. Daniel Murray, Pilot Study Co-Director, U.S. Environmental Protection Agency (USA)

11:15 Report on 2005 Meeting, **Professor Annik Magerholm Fet,** Department of Industrial Economics and Technology Management, Norwegian University of Science and Technology (Norway)

11:30 Lunch

13:00 CCMS and the Security through Science Programs
Mr. E. Sanguineti, *Public Diplomacy Division, Threats and Challenges Section, NATO Headquarters, Brussels, Belgium*

13:20 Sustainability and Green Chemistry
Prof. J. Swindall, *QUILL Research Centre, Belfast, Northern Ireland, UK*

13:40 Integration of a Sustainability Indicators Framework in Corporate Strategy
Drs. A. A. Martins, T. M. Mata, S. Sikdar, and C.A. V. Costa, *University of Porto, Portugal and Office of Research and Development, U.S. EPA, Cincinnati, OH, USA*

14:00	Approaches to Minimize Industrial Water Usage ***Prof. P. Glavič* and M. Bogataj,** *University of Maribor, Faculty of Chem. and Chem. Engineering, Maribor, Slovenia*
14:20	Coffee Break
14:50	Sustainable Processes in the Steel Industry in Flanders ***Dr. C. Block,*** *Leuven Engineering School GroepT, Leuven, Belgium*
15:10	Evaluation of Several Zeolites as Adsorbents for Sulfur Compounds by Inverse Gas Chromatography ***E. Díaz, S. Ordóñez, A. Vega, Prof. J. Coca,*** *Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain*
15:30	Open Discussion on Metrics for Sustainable Technologies ***Dr. Subhas Sikdar (Moderator)***
16:45	Adjourn
17:15	**Departure from outside the hotel for a Boat Tour on Bosphourus and dinner on board**

Tuesday, May 9, 2006 TECHNICAL EXCURSION

07:45 – 18:00 Departure from outside the hotel at 07:45

Field Trip/Industry Visits/Local Sights (by bus – Asian side of Istanbul)

- Visit to the TUBITAK- Marmara Research Center (MRC)
- Tour of the research laboratories at MRC (9:30 – 12:00)

- **Lunch at MRC (12:00 – 13:00)**

- Company Visit to GOODYEAR (tire production) (14:00-15:00)
- Company Visit to FORD (automobile production) (15:30-17:30)

Dinner at Ford Company (bus will go to downtown after dinner, strolling in Beyoglu-Taksim area)

Wednesday, May 10, 2006

SPECIAL TOPICAL SYMPOSIUM
"WATER REUSE AND RECYCLING"

08:30 Registration

09:00 Water Recycling and Reuse in EU Countries: Problems and Prospective
Dr. A. N. Angelakis, *Institute of Iraklio, National Agricultural Research Foundation, Iraklio, Greece* (could not attend due to a sickness)

09:45 U.S. EPA's Guidelines for Water Reuse
Mr. D. J. Murray, Jr., *U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, U.S.A.*

10:15 Coffee Break

10:45 Membrane Engineering in Water Reuse and Recycle
Prof. E. Drioli and A. Criscuoli, *Department of Chemical Engineering and Materials, University of Calabria, and Institute on Membrane Technology, ITM-CNR, Italy*

11:15 Treatment of Campus Wastewaters by Membrane Bioreactor for Potential Reuse in Irrigation
Assoc. Prof. Mehmet Kitiş, N.Ö. Yiğit, I. Harman, G. Civelekoglu, *Suleyman Demirel University, Department of Environ. Eng., Isparta, Turkey*

11:45 Textile Wastewaters: Water Reuse and Dyestuff Removal and/or Degradation
Assoc. Prof. G. P. Gallios, E.K. Dafnopatidou, E.G. Tsatsaroni, K.A. Matis, and N.K. Lazaridis, *Division of Chemical Technology, School of Chemistry, Aristotle University, Thessaloniki, Greece*

12:15 Lunch

13:30 Water Segregation and Reuse in Textile Industry
Dr. A. Baban, N. Kiran-Ciliz, G. Avaz, S. Murat, *TUBITAK - Marmara Research Center, Energy Systems and Environmental Research Institute, Gebze, Turkey*

14:00 Water Use, Reuse, and Recycling in Micro- and Nano-Manufacturing
Prof. F. Shadman, *Director of NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing, University of Arizona, Tuscon, AR, USA*

14:30 Studies on Some Selected Urban Wastewater Treatment Plant Effluents of Turkey to Search Their Reuse Potential in Agriculture
Prof. Ayşegül B. Tanık, *Istanbul Technical University, Environ. Eng. Department, Istanbul, Turkey*

15:00 Coffee Break

15:30 Water Saving, Reuse and Recycling in Industry: Cleaner Production Opportunities
Prof. J. Staniskis, *Institute of Environmental Engineering, Kaunas University of Technology, Kaunas, Lithuania*

16:00 Efficient Management of Wastewater, Its Treatment and Reuse in the Mediterranean Countries - EMWATER
Prof. G. Akçin, *Chemistry Department, Yildiz Technical University, Istanbul, Turkey*

16:30 Problems and Applications of Water Reuse in Israel
Prof. C. Forgacs, *The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva,Israel*

17:00 Improving Water QualityThrough Low-cost Upgrading of a Water Treatment Facility Accompanied by Abandonment of Chlorination
Prof. W.M. Zadorsky, ***B.V. Pismenny,*** *Ukrainian State University of Chemical Engineering, Dnipropetrovsk, Ukraine*

17:30 End of Technical Program

18:30 **Departure from outside the hotel for dinner at Kervansaray Restaurant**

Thursday, May 11, 2006

09:00 Treatment of the residual fraction of domestic waste: the Flemish case
Prof. C. Vandecasteele, *Department of Chemical Engineering, University of Leuven, Leuven, Belgium*

09:20 Treatment of Wastewaters through Adsorption of Heavy Metals by Natural Clay
Prof. K.T.Ewida, ***D.S.Elmonayeri, M.R.Ezz El. Din, M.S. Ghaly,*** *Environmental Engineering Dept, Faculty of Engineering Zagazig University, Zagazig, Egypt*

09:40 Industrial Wastewater Treatment: Metals Recovery and Water Reuse
Assoc. Prof. G.P. Gallios *et al., Division of Chemical Technology, School of Chemistry, Aristotle University, Thessaloniki, Greece*

10:10 Wastewater Treatment with Integrated Membrane-Electroflotation Method
Prof. G.G. Kagramanov, ***V.A. Kolesnikov, P.S. Sudilovskiy,*** *D.I. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia*

10:30 Coffee Break

11:00 Application of New Indexes for Comparing Membrane Operations to Traditional Techniques
Drs. A. Criscuoli and E. Drioli, *Institute on Membrane Technology, ITM-CNR, and Department of Chemical Engineering and Materials, University of Calabria, Italy*

11:20 Arsenic Removal from Waters Using Magnetically Modified Zeolite
Dr. M. Vaclavikova, ***G. Gallios, M. Matik, S. Jakabsky and S. Hredzak,*** *Institute of Geotechnics, Slovak Academy of Sciences, Kosice, Slovakia*

11:40 Color Removal from Textile Wastewaters by Changing Surface Properties of Adsorbent Material (Clinoptilolite)
Prof. A. T. Atimtay, ***Y.B. Duygulu,*** *Middle East Technical University, Environmental Engineering Department, Ankara, Turkey*

12:00 Lunch

13:30 Thermodynamic Modeling of Inorganic Chemical Species in Natural Polluted Waters
Assoc. Prof. S. Tepavitcharova, T. Todorov, D. Rabadjieva, *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

13:50 The National Cleaner Production Program: Benefits Assessment
Col. A. Komar, F.Bozek, and J. Dvorak, *University of Defence, Faculty of Economics and Management, Chair of Materials and Services, Brno, The Czech Republic*

14:10 Utilization of Cleaner Production and the Best Available Technology in a Food Processing Plant
Dr. F.Bozek, J. Kotovicova, A. Komar and J. Dvorak, *University of Defence, Faculty of Economics and Management, Chair of Civil Protection, Brno, The Czech Republic*

14:30 Enforcement of Environmental Regulations in Israel - 2005
Prof. C. Forgacs, *The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva,Israel*

14:50 Coffee Break

15:20 Urban Water Services Development - Romanian Perspective
Mr. V. Harceag, *National Company for Investments, Bucharest, Romania*

15:40 Cleaner Production Activities in Moldova
Mr. A. Stratulat, *Advisor for Prime Minister and Vice Prime Minister of the Republic of Moldova, Moldova*

16:00 Factors behind Cleaner Production in the Hungarian Manufacturing Industry - Results of a Survey
Mr. G. Harangozo, *Hungarian Cleaner Production Centre, Corvinus University of Budapest, Budapest, Hungary*

16:20 Carbon Dioxide Emissions in Spain: Main Sources and Capture Possibilities
Prof. J. Coca, *Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain*

16:40 Adjurn

19:00 **Conference Dinner at Baltalimani Restaurant (Farewell Dinner)**
(Departure from outside the hotel by bus at 18:00)

Friday, May 12, 2006

09:00 Networking Satellite Groundstations to Support Global Science: Toward a Distributed Shared Spatial Data Archive and Grid Access to Near-Real-Time Remote Sensing Data
Dr. G.L. Rochon, *Associate Vice President for Collaborative Research, Director of Purdue Terrestrial Observatory, Purdue University , W. Lafayette, IN, USA,*
V. Sharpton*, University of Alaska Fairbanks, Alaska, USA,* ***O.K. Ersoy,*** *Purdue University, USA*

09:20 Efficient Technology for Precious Metals Extraction from Secondary Raw Materials
Dr. A. Omelchenko, ***V. Y. Kotyegov, T. S. Kamalov, O. I. Shkola,*** *University of Manitoba, Winnipeg, Manitoba, Canada*

09:40 Red Mud – A Potential Sorbent for Removal of Heavy Metal Cations
Dr. M. Vaclavikova*, Institute of Geotechnics, Slovak Academy of Sciences, Watsonova, Kosice, Slovakia*

10:00 Presentations from **2007** Meeting Host Candidates

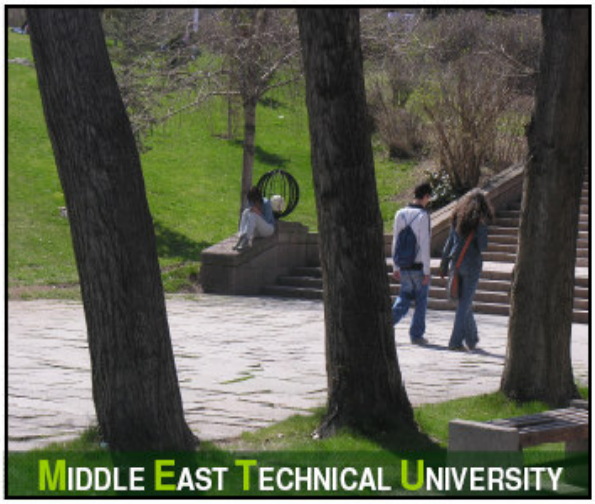
10:30 Coffee break

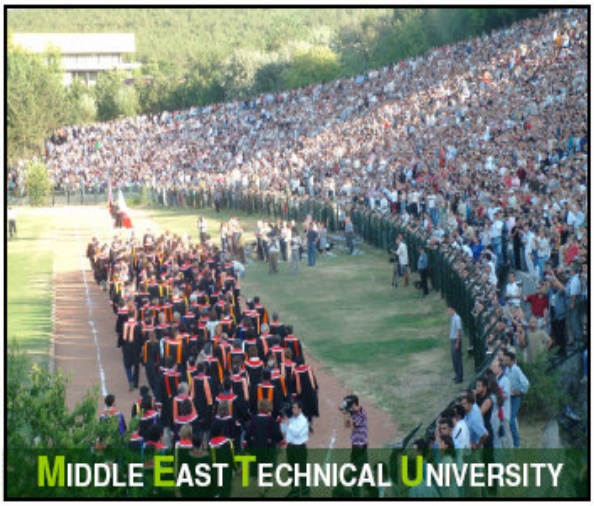
11:00 2007 Meeting Location Announcement and Discussion of Topics for the next Meeting, Mr. Daniel Murray and 2007 Meeting Host

12:00 Meeting Wrap Up, Dr. Subhas Sikdar

Bosphorous Bridge, Istanbul, Turkey

Opening Speech of the Vice Rector, Prof. Dr. Fatoş Y. Vural




MIDDLE EAST TECHNICAL UNIVERSITY

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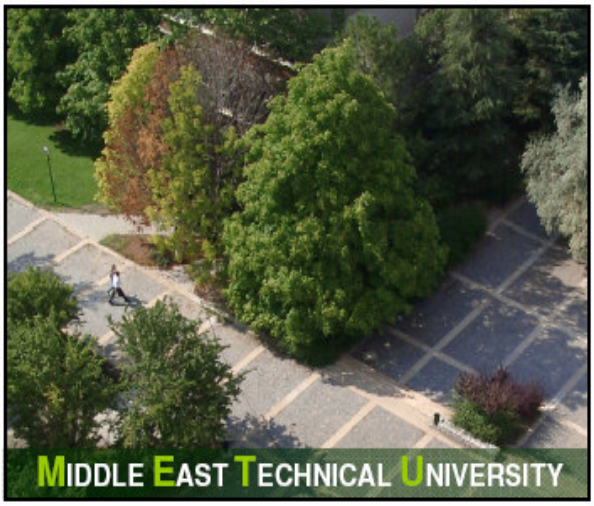
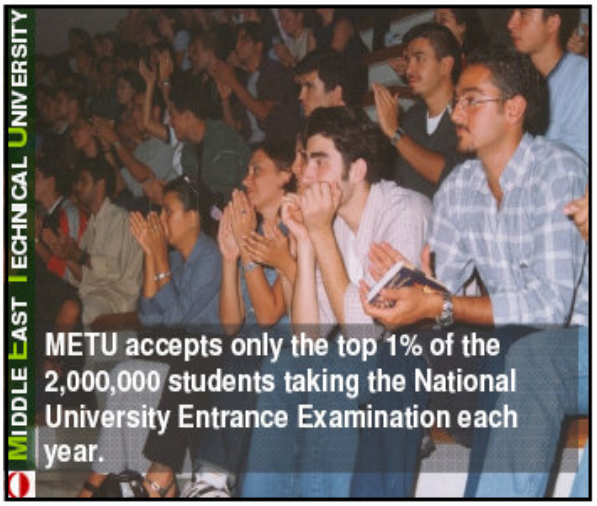
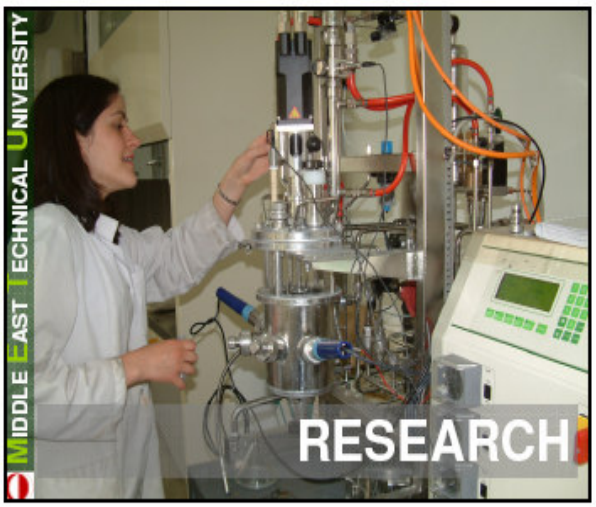

MIDDLE EAST TECHNICAL UNIVERSITY


MIDDLE EAST TECHNICAL UNIVERSITY
METU accepts only the top 1% of the 2,000,000 students taking the National University Entrance Examination each year.

MIDDLE EAST TECHNICAL UNIVERSITY
Enrolment of 15,000 undergraduate and 6,000 graduate students

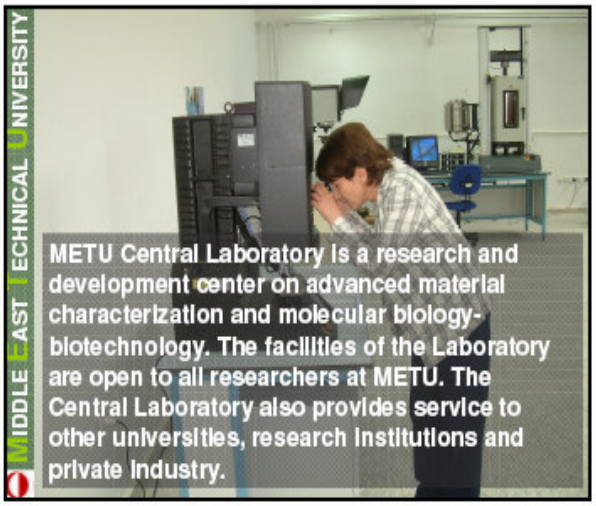
MIDDLE EAST TECHNICAL UNIVERSITY
More than 60 student clubs ranging from archaeology to bird-watching and ballroom dancing to astronomy


MIDDLE EAST TECHNICAL UNIVERSITY
RESEARCH

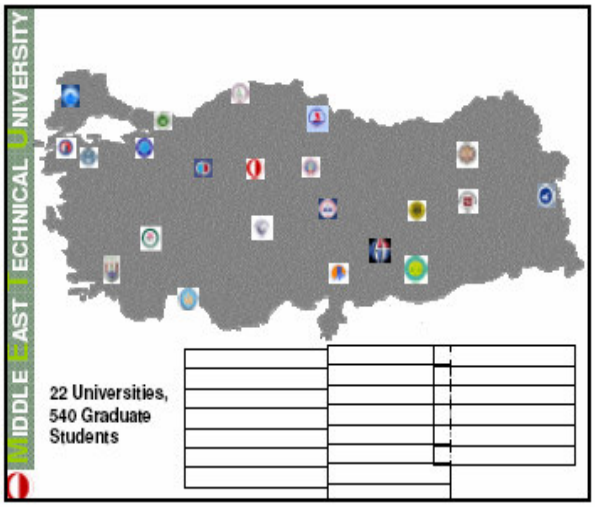
MIDDLE EAST TECHNICAL UNIVERSITY
Applied and theoretical research projects in a year reach 1,000, including the EU projects such as Framework Program, COST, Eureka etc.

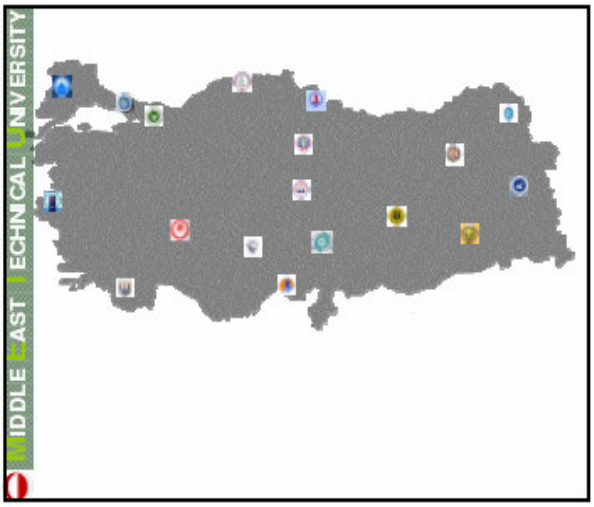
MIDDLE EAST TECHNICAL UNIVERSITY
RESEARCH CENTERS

CENTRAL LABORATORY
ODTÜ


MIDDLE EAST TECHNICAL UNIVERSITY
METU Central Laboratory is a research and development center on advanced material characterization and molecular biology-biotechnology. The facilities of the Laboratory are open to all researchers at METU. The Central Laboratory also provides service to other universities, research institutions and private industry.

MIDDLE EAST TECHNICAL UNIVERSITY
The objective for establishing the central laboratory is to supply state-of-the-art instrumentation for use by the research people at METU in order to promote collaboration among the researchers and strengthen the research activities.


MIDDLE EAST TECHNICAL UNIVERSITY
22 Universities,
540 Graduate
Students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MIDDLE EAST TECHNICAL UNIVERSITY
INTEGRATION TO ERA

MIDDLE EAST TECHNICAL UNIVERSITY
METU-Office of EU Affairs was established in 2000 with the aim of integrating Turkey with Europe, mainly in the areas of research, training and education.
An important mission of the Office is to help build a bridge between Europe and Asia, leading to Eurasian Research Area.

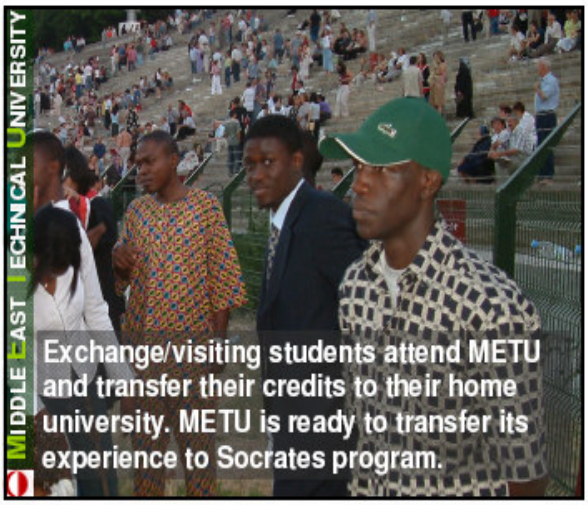
MIDDLE EAST TECHNICAL UNIVERSITY
SCIENCE AND TECHNOLOGY MUSEUM

MIDDLE EAST TECHNICAL UNIVERSITY
THE FIRST INTERNET SERVICE PROVIDER in TURKEY

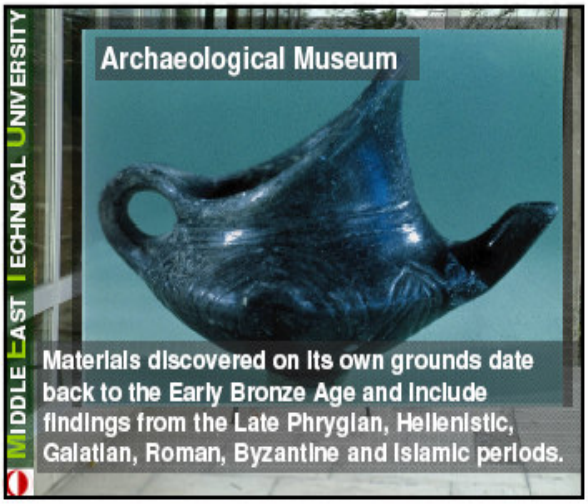
MIDDLE EAST TECHNICAL UNIVERSITY
METU TECHNOPOLIS

MIDDLE EAST TECHNICAL UNIVERSITY
METU has set aside 70 hectares for the first Technopolis in Turkey.

MIDDLE EAST TECHNICAL UNIVERSITY
INTERNATIONAL UNIVERSITY


MIDDLE EAST TECHNICAL UNIVERSITY
Exchange/visiting students attend METU and transfer their credits to their home university. METU is ready to transfer its experience to Socrates program.

MIDDLE EAST TECHNICAL UNIVERSITY
LIBRARY


MIDDLE EAST TECHNICAL UNIVERSITY
Archaeological Museum
Materials discovered on its own grounds date back to the Early Bronze Age and include findings from the Late Phrygian, Hellenistic, Galatian, Roman, Byzantine and Islamic periods.

Mission of Clean Products and Processes

- Promote cooperation for improving the common pollution landscape by stimulating cross-national dialogues and collaboration
- Share knowledge on the methods, tools, and technologies for making cleaner and sustainable products and processes possible.

Clean Products and Processes

- Rational product design using life cycle assessment
- Measuring pollution or wastes in processes, and minimizing them at the enterprise level
- Green chemistry and processing/ Material substitution
- Improving energy efficiencies
- Efficient separation technologies
- Sustainability and Metrics
- Effective dissemination of technical knowledge

Annual Meeting Activities

- Invited speakers on innovative technologies
- Topical Conference (one-day)
  - Product design (Copenhagen)
  - Process design (Oviedo)
  - Industrial ecology (Vilnius)
  - Process Intensification (Cetraro)
  - Environmental Education (Budapest)
  - Marine Biotechnology (Alesund)
- Computer Café and Posters
- Updates on country-sponsored projects
- Tour de Table
- Visits to exemplary industrial sites

Clean Products and Processes

First meeting in Cincinnati, US (March 1998)

Second meeting in Belfast, Northern Ireland, UK (March 1999)

Third meeting in Copenhagen, Denmark (May 2000)

Fourth meeting in Oviedo, Spain (May 2001)

Fifth meeting in Vilnius, Lithuania (May 2002)

Sixth meeting in Cetraro, Italy (May 2003)

Seventh meeting in Budapest, Hungary (May 2004)

- Initially 14 Countries,now 31 countries (including NATO and non-NATO European), Israel, and Egypt
- CCMS Fellows from Portugal, Turkey

Products from this Pilot

- Annual Reports (hard copies and web-based)
- Clean Production Evaluation in member countries (metal finishing, textiles, food/agricultural, etc.)
- Portal-site on EPA website on clean production information
- Journal Papers from Topical Sessions

Phase I Projects in the Pilot

1. Pollution Prevention Tools (USA) – On schedule and ongoing
2. Water Conservation and Recycling in Semiconductor Industry: Control of Organic Contamination and Biofouling in Ultra Pure Water Systems (USA and UK) - Complete
3. Clean Products and Processes in Textile Industry (USA) - Complete
4. Clean Processes in the Turkish Textile Industry (Turkey) - Complete
5. Energy Efficiency in Moldova (Moldova) - Abandoned

Phase I Projects in the Pilot - cont'd

6. Cleaner Energy Production With Combined Cycle Systems (Turkey) - Ongoing
7. The Danish Center for Industrial Water Management Update. A Case on: LCA of Alternative Scenarios for Water Reuse in Molded Pulp Production (Denmark & Turkey) - Complete
8. International Exchange and Dissemination of Clean Products and Processes Information: Within the Pilot Study and to Industry and the Public (USA & Germany) - Incomplete
9. Fellow Projects (Portugal) - Complete
10. Use of Intelligent Systems in Pulp and Paper Industry (Canada) - Abandoned

Current Projects in the Pilot

- Environmental management of industrial park by Israel, Turkey, Poland, Hungary, Denmark, and Lithuania.
- Hybrid membrane application (milk, olive oil, chemicals) by Spain, Russia, Italy, Poland, Denmark
- Agricultural ecology by Israel
- Sustainability indicators benchmarking by Germany, Norway, Hungary, Lithuania, USA
- Medical care (hospitals, diagnostic facilities that use radionuclides) by Czech Republic

Spin-off Activities

- U.S. EPA and University of Porto, Portugal
- Jim Swindall (UK) guidance on University-Industry Cooperative Research Centers
- University of Oviedo (Spain) , Mendeleev University in Moscow, and U.S. EPA
- University of Calabria (Italy) and US EPA
- Purdue University set up Real Time Remote Sensing & Environmental Monitoring Centers of Excellence Project with partners in Belgium, Bulgaria, Canada, Croatia, Egypt, Georgia, Greece, Spain, Turkey, Ukraine, and the United States

SPIN-OFF PROJECTS: DTU

- Denmark Technological University and Solutia (USA)
- DTU and Kaunas University, Lithuania
- DTU and Questor, Northern Ireland, UK
- DTU and Masmara Research Center, Turkey
- DTU and US EPA
- DTU and North Carolina State U (USA)
- DTU and Tech U of Tessaloniki (Greece)
- DTU and U of Natal (South Africa)

Thanks to the meeting organizers and hosts of the last several years:

- Steve James (USA) for Cincinnati, '98
- Prof. Jim Swindall (UK) for Belfast, '99
- Prof. Henrik Wenzel (Denmark) for Copenhagen, '00
- Prof. José Coca (Spain) for Oviedo, '01
- Prof. Jurgis Staniskis (Lithuania) for Vilnius, '02
- Prof. Enrico Drioli (Italy) for Cetraro, '03
- Gyula Zilahy (Hungary) for Budapest, '04
- Annik Fet (Norway) for Alesund, '05

NATO/CCMS Pilot Study on Clean Products and Processes
2006 Annual Meeting
Program Overview

Daniel J. Murray, Jr. P.E.
U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Cincinnati, Ohio

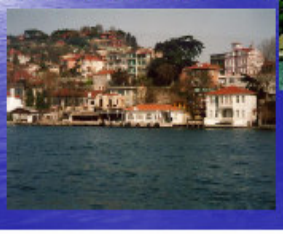
A Look at the Week Ahead

- Today – technical presentations & open discussion of sustainable technology metrics
- Tuesday – field trip, research center tour, industry visits & local sights
- Wednesday – topical symposium on water reuse and recycling
- Thursday – national delegate technical presentations
- Friday – technical presentations, selection of 2007 host & wrap up

Today

- Summary of 2005 Meeting
- CCMS and Security through Science Programs
- Technical Presentations – sustainability in industrial processes, corporate management and chemistry
- Open Discussion – sustainable technology metrics

Tour on the Bosphorus



Tuesday

- Field Trip
  - –TUBITAK – Marmara Research Center
  - –Industry Visit – Goodyear Tire
  - –Industry Visit – Ford Automotive

TUBITAK – Marmara Research Center

Goodyear Tire

Ford Automotive

Wednesday

- Topical Symposium: Water Reuse and Recycling
  - EU, U.S., Mediterranean Region, Israel Programs
  - Membrane applications
  - Sector applications – textiles, micro-nano, agriculture

Thursday

- Delegate Technical Presentations
  - wastewater treatment,
  - membranes,
  - chemical modeling,
  - carbon dioxide emissions,
  - several national perspectives on cleaner production and related issues

Friday

- Technical Presentations
  - Remote sensing data exchange
  - Metals recovery and removal
- 2007 Host Candidate Presentation and Selection
- 2007 Meeting Topics and Focus
- Meeting Wrap Up

NATO/CCMS Pilot Study on Clean Products and Processes 2005 Annual Meeting

Ålesund, Norway
19-24.June 2005

Outline

- Professional Progam
- Special Topic Seminar
- Social Activities
- Results, follow-up activities

Venue, participants

- High number of participants representing a large number of countries: 38 participants from 26 countries;
- Venue: Ålesund University College in collaboration with the Norwegian University of Science and Technology

Professional Progam

- Presentations from each delegate
- Special Invited Speakers
- Topical Symposium

Norwegian Minister of Defence Kristin Krohn Devold:

Environment and Security:

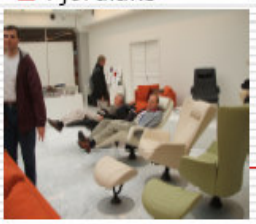
Two sides of a Coin in Order to Achieve a Sustainable Future

Topical Symposium

- Focus: **Environmental Challenges in Marine Biotechnology, Product Design and Innovation**

Industry visits

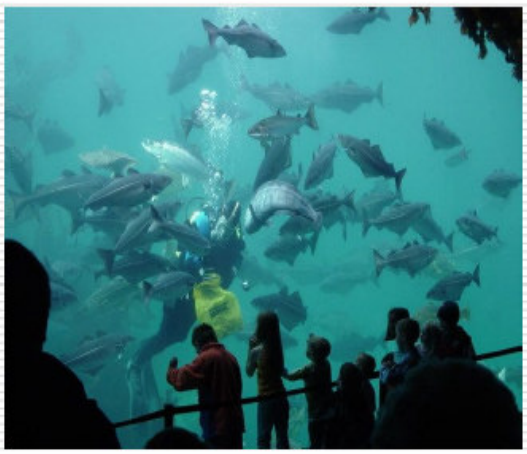
- Ulstein Shipyard
- Hjellegjerde
- Sandella
- Fjordlaks



Social Activities

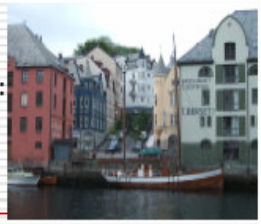
- Boat trip to the industry sites
- Guided tour and party at the Sunnmøre Museum
- Midsummer cruise with "Keiser Wilhelm", baccallao dinner, singing and dancing
- Ålesund Aquarium

GUIDE



Results, follow-up activities

- Discussions, joint project ideas
- Journal of Clean Technologies and Environmental Policy:
  - received: 8 articles
  - to be published: Fall, 2006



CCMS AND THE SECURITY THROUGH SCIENCE PROGRAMS

Emanuele Sanguineti

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Abstract

The science and society element of the Third Dimension of NATO is under two programmes:

- Security Through Science
  - Science Committee
- Environment and Society
  - Committee on the Challenges of Modern Society (CCMS)

The Committee on the Challenges of Modern Society has been created as a **forum for sharing of knowledge and experience** on technical, scientific and policy aspects of social and environmental matters in both the civilian and military sectors among NATO[1] and Partner countries[2], as well as NATO-Russia, Mediterranean Dialogue countries[3] and joint NATO-Ukraine working group on Science and Environment.

The work is carried out on a **decentralized basis** and **participation by nations is voluntary.**
The **activities** sponsored by CCMS are:

- **Pilot Studies** (3-5 years)
- **Short Term Projects** (12-24 months)
- **Topical workshops** (single events

In 2000, 5 Key Objectives were adopted by the Committee:

- Reducing the environmental impact of military activities
- Conducting regional studies including cross-border activities
- Preventing conflicts in relation to scarcity of resources
- Addressing emerging risks to the environment and society that could cause economic, cultural and political instability
- Addressing non-traditional threats to security

Activities within the framework of CCMS are organized in NATO and Partner countries.

Internet Addresses are: http://www.nato.int/science , http://www.nato.int/ccms/

[1] Belgio, Bulgaria, Canada, Danimarca, Estonia, Francia, Germania, Grecia, Italia, Islanda, Lettonia, Lituania, Lussemburgo, Norvegia, Olanda, Pologna, Portogallo, Regno Unito, Repubblica Ceca, Romania, Slovacchia, Slovenia, Spagna, Turchia, Ungheria, USA.
[2] Albania, Armenia, Azerbaijan, Bielorussia, Croazia, Gerogia, Kazakistan, Kyrgistan, Macedonia, Moldavia, Tajikistan, Turkmenistan, Ucraina Uzbekistan.
[3] Algeria, Egitto, Giordania, Israele, Marocco, Mauritania, Tunisia.

A Unique Network of Cooperation

NATO countries

Belgium, Bulgaria, Canada, Czech Republic, Denmark, Estonia, France, Germany, Greece, Hungary, Iceland, Italy, Latvia, Lithuania, Luxemburg, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Turkey, UK, US

Partner countries

Russia, Ukraine, Belarus, Moldova, FYROM, Finland, Sweden, Ireland, Austria, Switzerland, Croatia, Albania, Georgia, Azerbaijan, Armenia, Kyrgyz Republic, Kazakhstan, Turkmenistan, Uzbekistan, Tajikistan

Mediterranean Dialogue countries

Algeria, Egypt, Israel, Jordan, Mauritania, Morocco, Tunisia

TOTAL: 53 Countries

NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

9th Annual Meeting of NATO-CCMS on Clean Products and Processes

CCMS and the Security through Science Programmes

NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

Emanuele Sanguineti, NATO Public Diplomacy Division, Threats and Challenges Section

NATO's third dimension

- The science & society element of the Third Dimension is under **two programmes**:
  - **Security Through Science**
    - Science Committee
  - **Environment and Society**
    - Committee on the Challenges of Modern Society (CCMS)

NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

NATO CCMS

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NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

NATO CCMS

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NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

CCMS Key Objectives

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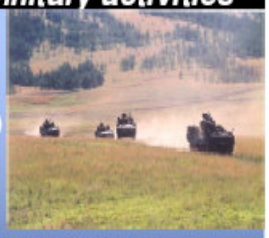
- Addressing non-traditional threats to security

NATO PUBLIC DIPLOMACY / OTAN DIPLOMATIE PUBLIQUE

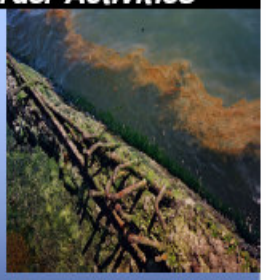
Reducing the environmental impact of military activities

- Workshop
  "Environmental Management System in the Military Sector"
  (Tbilisi, Georgia 5-6 October 2006)
- Workshop"Sustainable Building for Military Infrastructure"
  (Switzterland will host the follow-up meeting in 2007)
- Workshop
  "Environmental Aspects of Military Compounds"
  (Vienna, Austria 9-11 May 2006)



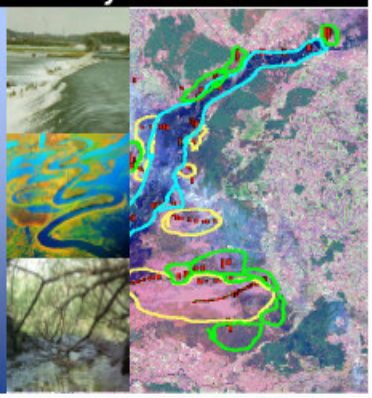
Regional Studies Including Cross Border Activities

- Pilot study
  "Ecosystem Modelling of Coastal Lagoons for Sustainable Management"
  (Oalidia lagoon, Morocco, 19-23 June 2006)
- Short term project
  "Management of Industrial and Toxic Wastes and Substances Researches"
  (Ioannina, Greece, August 26-27, 2006)



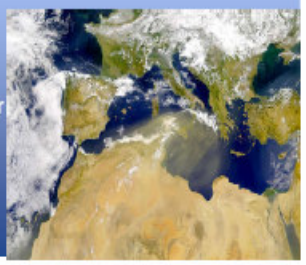
Prevention of Conflicts in Relation to Scarcity of Resources

- Pilot study
  "Integrated Water Management"
  (Warsaw, Poland
  June 1-5, 2006)



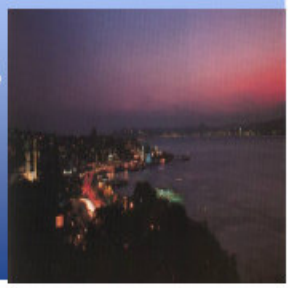
Emerging Risks to the Environment and Society

- Pilot study
  "Prevention and Remediation Issues in Selected Industrial Sectors"
  (Athens, Greece, June 4 - 7, 2006)
- Pilot study
  "Using Landscape Science for Environmental Assessment"
  (St. Petersburg, Russia,
  July 3 - 6, 2006)



Non-Traditional Threats to Security

- Pilot study
  "Food Chain Security"
  Helsinki, Finland, May 4-5, 2006)
- Pilot study
  "Security of Narrow Waterways, Ports/Harbours and Adjacent Populated Areas
  (Completed in 2005)



Security through Science Programme (STS)

- The aim of the STS Programme is to contribute to security, stability and solidarity among nations by applying science to problem solving
- **BOTTOM UP approach**:
  Grants are offered to scientists in NATO, Partner and Mediterranean Dialogue countries to collaborate on priority research topics

STS Priority Research Topics

- Defence Against Terrorism
  - Rapid Detection of CBRN Agents and Weapons, and Rapid Diagnosis of their Effects on People
  - Novel and Rapid Methods of Detection
  - Physical Protection against CBRN Agents
  - Decontamination of CBRN Agents
  - Mediacal Countermesoures
  - Explosive Detection
  - Eco-Terrorism Countermesoures
  - Computer Terrorism Countermesoures

STS Priority Research Topics

- Scientific Collaboration to Counter other Threats to Security
- Environmental Security (e.g. desertification, land erosion, pollution, etc.)
- Water Resources Management
- Management of Non-Renewable Resources
- Modeling Sustainable Consumption (e.g. energy, materials, etc.)
- Disaster Forecast and Prevention
- Food Security
- Information Security
- Human and Societal Dynamics (e.g. economic impact of terrorist actions)

STS Priority Research Topics

- Partner Country Priorities
  - Specific topics for collaborative research have been identified by the Partner countries
  - Themes:
    - Environmental Security
    - Computer Networking
    - Counter Terrorism

Updated list is posted on the Science website
www.nato.int/science

Organization: Four Advisory Panels

- Chemical / Biological / Physics
  CBP Panel
- Information and Communications Security
  ICS Panel
- Environmental Security Panel
  ESP Panel
- Human and Societal Dynamics Panel
  HSD Panel

Environmental Security Panel

RELEVANT PRIORITY RESEARCH TOPICS

Defence Against Terrorism
- Eco-Terrorism Countermeasures
- Decontamination of CBRN

Countering Other Threats to Security
- Environmental Security (e.g. desertification, pollution)
- Water Resources Management
- Management of Non-Renewable Resources
- Modelling Sustainable Consumption (e.g. food, energy, materials)

Partner Country Priorities

Funding mechanisms

- Advanced research Workshops (ARW)
- Advanced Study Institutes (ASI)
- Collaborative Linkage Grants (CLG)
- Expert Visits (EV)
- Reintegration Grants (RIG)
- Science for Peace projects (SFP)

STS Support Grants

- **Advanced Research Workshop (ARW)**
  - Grants to organise expert workshops where an intense but informal exchange of views at the frontiers of a subject aims at identifying directions for future action
    - Upper limit 35,000 Euro (exceptional hard limit: 50,000 Euro)
- Advanced Study Institutes (ASI)
  - Grants to organize high-level tutorial courses to convey the latest developments in a subject to an advanced-level audience
    - Upper limit 40,000 Euro

STS Support Grants

- **Collaborative Linkage Grants (CLG)**

To pool ideas and resources on research projects, and create specialist network

- Upper limit 30,000 Euro

- **Expert Visits (EV)**

Grants to allow the transfer of expertise in an area of research through providing assistance with ongoing research project

- Upper limit 5,000 Euro

STS Support Grants

- **Reintegration Grants (RIG)**

To allow young scientists from Partner countries working in NATO countries abroad to return and reintegrate into the research communities of their home countries

- Three years grant of approximately 20,000 Euro (10,000 Euro for grantee - 10,000 Euro for institution)

- **Science for Peace projects (SfP)**

Offer support for research and development projects in Partner and Mediterranean Dialogue countries, to cover project related costs

- Average NATO funding 300,000 Euro

Examples of Activities sponsored by ESP Panel in 2006

- ARW "Solar Desalination for the 21st Century" (Italy/Egypt)
- ASI "Advanced Modelling Techniques for Rapid Diagnosis and Assessment of CBRN Agents Effects on Water Resources" (Turkey/Kyrgyz Republic)

STS and CCMS website

- Offers the opportunity to search for information on NATO/CCMS and StS activities
- Provides access to information and online publications

Internet Addresses

http://www.nato.int/science
http://www.nato.int/ccms/

Thank you for your kind attention

SUSTAINABILITY AND GREEN CHEMISTRY

Jim Swindall

QUILL Research Centre, David Keir Building, Stranmillis Road, Belfast BT9 5AG Northern Ireland, UK (j.swindall@qub.ac.uk)

Abstract

The background to the newly formed G8 International Green Network (IGN) will be outlined with details of the programme during the first four years.

The recent award of a Queen's Anniversary Prize for Higher and Further Education to QUILL will also be highlighted with a brief discussion of how the IGN and the Prize has stimulated a major initiative in Queen's University to establish an Institute of Sustainability.

"Green Chemistry and Sustainability"

Professor Jim Swindall OBE
Director QUILL Research Centre
The Queen's University of Belfast

NATO CCMS, Istanbul 7 – 12th May 2006

- Carnegie Meeting of G8 Science Ministers
- Canada, France, Germany, Italy, Japan, Russia, UK, USA
- Italy chaired June 2005 meeting in Montreal and proposed Green - Sustainable Chemistry as a suitable project for support
- The project to be called "International Green Network" was ratified at the New York meeting last December

International Green Network

- Pietro Tundo of INCA in Venice is the Director of the Network
- Ken Seddon, QUILL Director, is the Deputy Director
- Approx $3 million over 4 years for each node
- QUILL gets extra $1 million to help organise the network

Primary Goals

A cleaner and safer environment through:

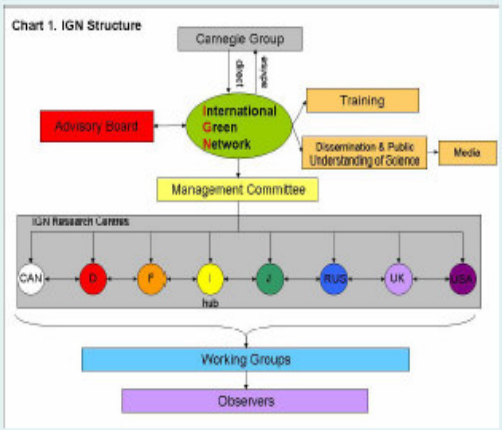
- The proliferation of research
- High-level capacity building in science
- The improvement of regulatory frameworks and public policy design
- the enhancement of public outreach and education

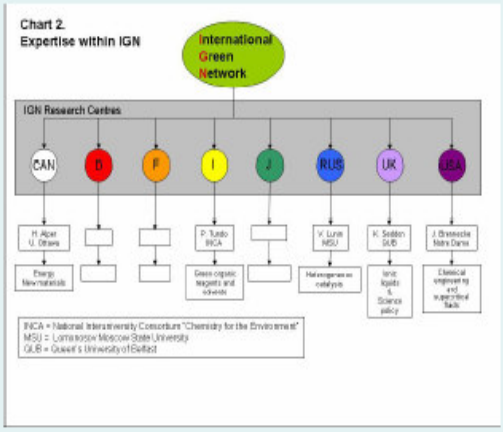
The IGN will address key policy issues by:

- Developing policy tools to encourage research, commercialisation and deployment of various sustainable energy and materials technologies
- Ensuring the adjustment of existing regulatory regimes in the energy and materials fields to encourage innovation and performance improvements that point towards sustainability

and by:

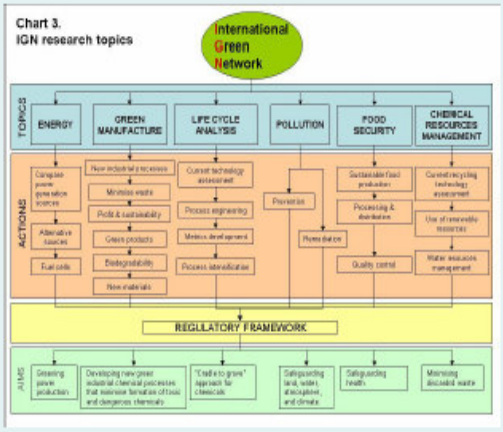
- Developing incentive structures that reward early movers and encourage progress towards sustainable energy and materials initiatives
- Developing policies to promote public education and debate around issues related to the energy and materials sector





Research Topics

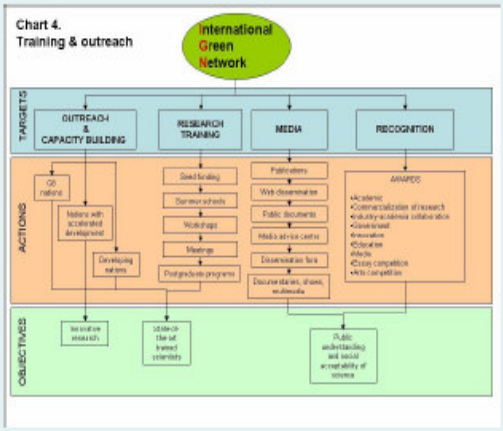
- Energy
- Green manufacture
- Life cycle analysis
- Pollution
- Food security
- Chemical resources management



Training and Outreach

Key priorities

- *Training of scientists,*
- *Outreach towards developing nations*
- *Dissemination*



Currently

- Awaiting funding confirmation from all 8 countries
- Hope to commence this summer

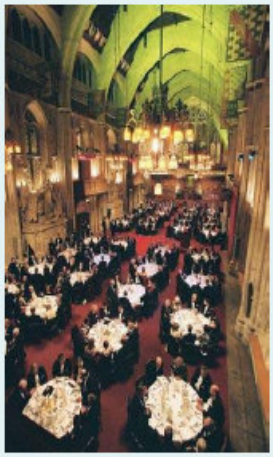
Award for QUILL

- The Queen's Anniversary Prizes for Higher and Further Education 2006
- Established in 1992 and awarded 6 times
- 21 prizes awarded each cycle
- Queen's has won 4 times, a feat matched by only 3 other UK universities
- QUESTOR won in 1996

Prize Citation

"The University's Ionic Liquid Laboratories are the premier world centre in the field, delivering pioneering research that is assisting the UK chemical industry in moving to cleaner, greener, and more profitable production. An outstanding example of industry-university collaboration, the development of 'ionic liquids' is a significant UK-led achievement providing solutions for one of the primary sources of pollution."

The GUILDHALL, London



Buckingham Palace, London

The Athenaeum Club, London

BP Headquarters
St. James Square

L'Escargot Restaurant

Something Else

- Last March 22nd Ceres announced the First-Ever Ranking of 100 Global Companies on Climate Change Strategy as follows:

"BP and DuPont Receive Top Scores in First-Ever Ranking of 100 Global Companies on Climate Change Strategies"

Ranking

Sector: Oil/ Gas, **Leader:** BP(90 points*), **Laggard:** ExxonMobil(35)

Sector: Chemical, **Leader:** DuPont(85**), **Laggard:** PPG(21)

Sector: Metals/Mining, **Leader:** Alcan(77) & Alcoa(74), **Laggard:** Newmont(24)

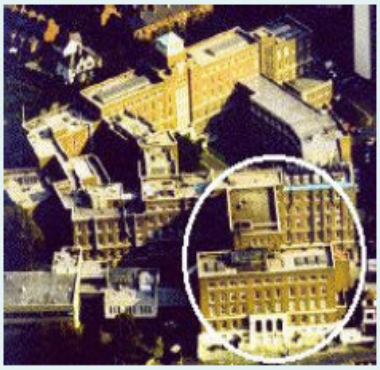
Sector: Electric Power, **Leader:** AEP & Cinergy(both73), **Laggard:** Sempra Energy(24)

Sector: Auto, **Leader:** Toyota(65), **Laggard:** Nissan(33)

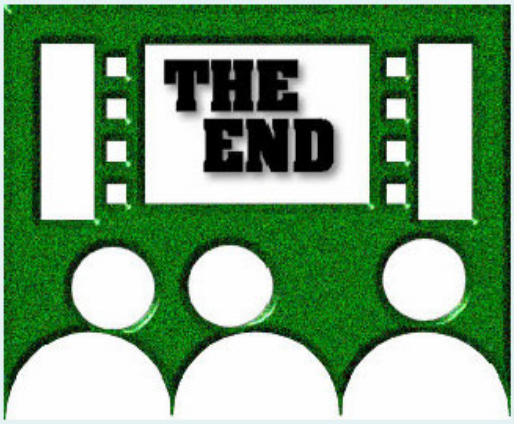
* Top score worldwide ** Top score among 78 US companies

Sustainability Initiative

- As a result of the G8 and the prize
- V-C seeking £30 million from donors to build a world class institute for sustainability
- Cross Faculty Initiative
- David Keir Building
- WISE – World Institute for a Sustainable Earth



FOTOSEARCH


THE
END

INTEGRATION OF A SUSTAINABILITY INDICATORS FRAMEWORK IN CORPORATE STRATEGY

António A. Martins [1], **Teresa M. Mata** [1], **Subhas Sikdar**[2], **Carlos A. V. Costa** [1]

[1] Chemical Engineering Department, Faculty of Engineering of the University of Porto, Portugal, (*amartins@fe.up.pt*, *tmata@fe.up.pt*, *ccosta@fe.up.pt*),
[2] *Office of Research and Development, United States Environmental Protection Agency (EPA), Cincinnati, OH, USA, (sikdar.subhas@epamail.epa.gov)*

Abstract

Nowadays there is a large consensus that sustainability is one of the most important and challenging topics involving the social, economic and ecological spheres. Although it is recognized that the transition towards sustainability will take some time and will require the active participation of many different players in different levels of society, there is still a lot of discussion on a number of important questions, in particular how progress towards sustainability is measured or assessed, what are the best strategies, how the different dimensions of sustainability can be related with each other.

At the core of these questions lie fundamental differences in the views, goals and solutions to the same problems from the different players at the political, social and economic levels. A classical example is the existence of an enormous quantity of environmental regulations that companies must follow, which they view as a problem that could potentially affect their long term competitiveness. However, there is a social pressure to improve the quality of the environment, which in many cases requires the imposition of strict rules and regulations.

One way to address these problems is through the definition of models and indicators including the different aspects of sustainability. These can be very helpful to measure the state and evolution towards sustainability and to decisions support. However, the existing frameworks are normally well-adjusted for specific areas, considering only part of the overall problem and they are not easily applied in strategic planning and management. A consistent framework should consider the particularities of the system studied, be based on basic principles of sustainable development and be enough flexible to be used in their different spheres: political, social and economic.

Sikdar[1,2] proposed a framework for incorporating sustainability principles through the use of appropriate quantitative metrics, with a special emphasis in manufacturing systems. It is based on a top down approach applicable to the company or process levels and defines three levels of sustainability indicators: (i) 3-D indicators that include simultaneously the three dimensions of sustainability: social, economic and environmental; (ii) 2-D indicators that include two dimensions of sustainability, e.g., socio-economic, eco-efficiency or socio-ecological indicators; and (iii) 1-D indicators that include just one dimension of sustainability, e.g., economic, ecological or social indicators. The proposed framework uses the 3-D indicators as decision making tools and considers the 2-D and 1-D indicators to address and answer specific issues and problems. This framework was applied by Martins *et al.*[3] to asses and compare the sustainability of chemical process. The results showed that the proposed methodology can be applied, using data easily available from the process or external sources.

This study builds on these previous results to extend the sustainability framework to assist in the measurement of a company environmental performance, its strategic management and performance, considering the different aspects of sustainability. In particular, it focuses on the relations between the strategy proposed by Sikdar and the Balanced Scorecard (BSC)[4] methodology discussing how they may interrelate.

The BSC methodology was originally conceived to help companies develop strategies to include the four main areas of their business: financial, costumers, process and learning. Because it also demands the definition of indicators to quantify the company performance and to take into account the different dimensions of the business, it shares similarities with the sustainability metrics framework. This work also presents and discusses the way both frameworks may complement and support each other.

References

1. Sikdar, S.K., Journey Towards Sustainable Development: A Role for Chemical Engineers, *Environmental Progress*, 22, 4, December, 2003: 227-232.
2. Sikdar, S.K., Sustainable Development and Sustainability Metrics, *AIChE Journal*, 49, 8, August, 2003: 1928-1932.
3. Martins, A.A., Mata, T.M, Sikdar, S.K., Costa, C. A Framework for Sustainability Metrics, Presentation made at the NATO CCMS meeting "Clean Products and Processes, Aalesund, Norway, 23 June, 2005.
4. Kaplan, D., Norton. D., "The Balanced ScoreCard: Measures that Drive Performance", *Harvard Business Review*, January-February 1992.

NATO CCMS Pilot Study
on Clean Products and Processes
Istambul, Turkey, 2006

Integration of a Sustainability Indicators Framework in Corporate Strategy

António Martins, Teresa Mata, Subhas Sikdar, Carlos Costa

U.PORTO

Importance

Organizations and companies are operating in an ever increasing competitive environment. Demands placed on them include:

- Reduced costs, increase efficiency and profitability
- Deliver the most value to their stakeholders and shareholders.
- Be socially and environmentally responsible

Importance

To be successful, a company or organization should

- Know the needs of the different stakeholders and costumers.
- Positioned itself market where it will be doing business.
- Provide the products or services aimed to the segments and costumers it is aiming.

Importance

To be successful, a company must devise a coherent and consisting strategy based in concrete goals.

- However there is still too much emphasis on the financial aspects.

- Interrelations between the financial, social and environmental spheres are normally neglected.

Importance

Other difficulties are:

- Social and environmental aspects are difficult to measure.

  They represent intangible assets, costs and liabilities.
- What social and environmental aspects are really important for a company/organization?

Balanced ScoreCard

When defining their strategy organizations must balance all aspects of their activities.

Balanced ScoreCard (BSC), first proposed by Kaplan and Norton, is a way to do this.

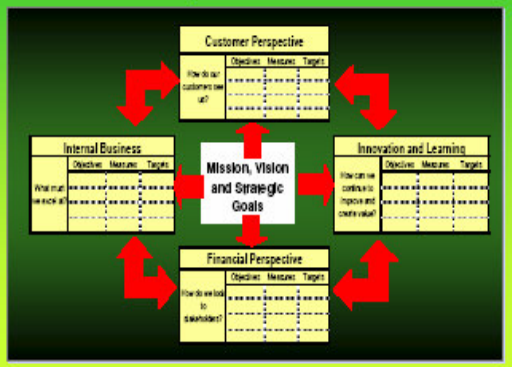
The BSC tries to reach a balance between tangible and intangible assets and drivers among the areas essential to the performance of an organization.

Balanced ScoreCard

The BSC is centred in the vision and strategic goals of an organization, and divides its activities in four main perspectives.

- Financial
- Customer relationships
- Internal process and
- Innovation, learning and information systems

Balanced ScoreCard



Balanced ScoreCard

The BSC starts by identify the relevant aspects of each of the perspectives, in a top down approach

- Financial and costumer relationships considered to be short term aspects.

- Internal processes and learning are considered to be long term dimensions and essential to the performance and success of the organization.

Balanced ScoreCard

Balanced ScoreCard

After the main aspects and drivers are identified, the relation between them are assessed.

- Based in cause-effects relations, quantified by indicators.
- From the bottom (learning and internal processes) to the top (customer relationship and financial perspectives).

Integration Indicators Framework

Sustainability issues should be integrated at the lower levels (internal processes and learning dimensions).

- They will have the most impact in the long term.
- Ensure that the activities of the organization consider all aspects of sustainability in a consistent way.

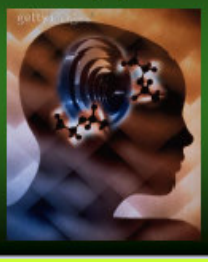
Integration Indicators Framework

Martins et al. proposed a framework of sustainability indicators. It can be used to complement the BSC, in particular:

- Help in the integration of sustainability in an organization's strategy.
- Determine what aspects of sustainability are relevant and must be considered by the organization.

Integration Indicators Framework

- Help the selection of appropriate indicators, based on the proposed hierarchy.



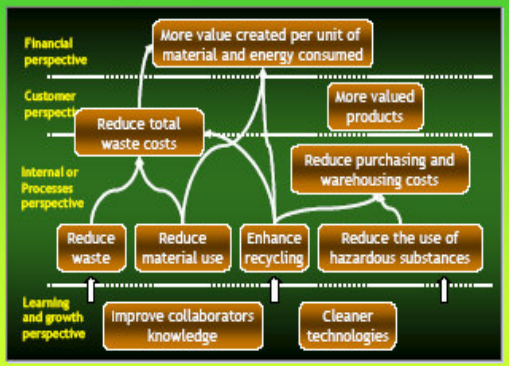
- Help in the definition of the correct cause and effect relations between various aspects.

Indicators Framework Integration

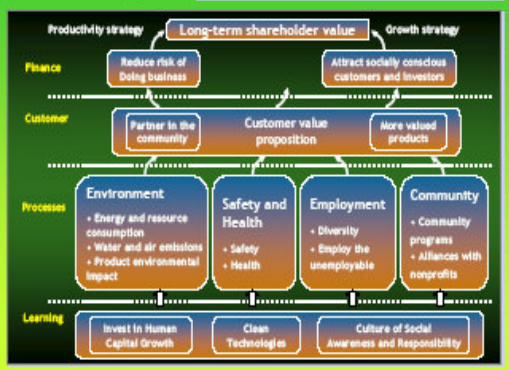
Two different strategies can be devised to complement the original BSC

- Define a new perspective that incorporate the sustainability aspects relevant to the organization activities.
- Incorporate them directly in the existing perspectives, specially in the lower ones.

Definition of an extra perspective



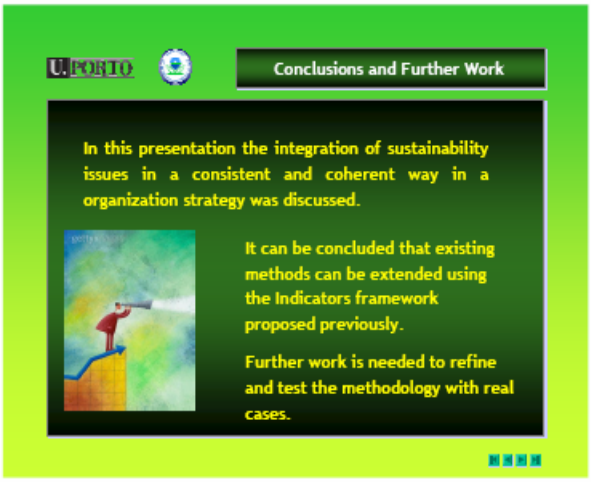
Direct integration

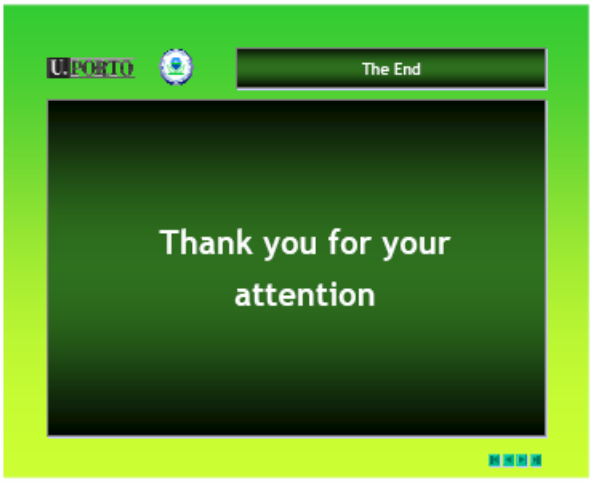


Indicators Framework Integration

3D indicators of energy and material intensity are natural choices for the aspects related with waste, consumption of energy and materials

3D indicators of chemical risk and potential environmental impact assess the product environmental impact and reductions on the use of dangerous materials and work accidents.


U.PORTO
Conclusions and Further Work
In this presentation the integration of sustainability issues in a consistent and coherent way in a organization strategy was discussed.
It can be concluded that existing methods can be extended using the Indicators framework proposed previously.
Further work is needed to refine and test the methodology with real cases.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Thank you for your attention

APPROACHES TO MINIMIZE INDUSTRIAL WATER USAGE

Peter Glavič, Miloš Bogataj

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Abstract

Fresh water supplies are diminishing while the demand is dramatically growing at an unsustainable rate. Over the next 20 years, the average supply of fresh water volume per capita is expected to drop by a third worldwide. Being one of the largest water consumers, chemical and process industries are therefore forced to look for solutions simultaneously reducing water consumption and water pollution.

Awareness of water scarcity, current drives towards sustainable development (e.g. IPPC directive (EU), Responsible Care (worldwide)) and rising costs of fresh water as well as rising effluent treatment costs have contributed to development of several novel techniques for minimizing water usage. Substantial reduction in fresh water intake can be achieved by means of wastewater reuse, recycling, regeneration, treatment and good water management practice.

One major area of research, initiated by Robin Smith from UMIST led to development of graphical targeting method which became known as "water pinch". The method is based on constructing a unique water limiting profile from which minimum overall water consumption can be determined. From its beginnings in late 1980's continuous improvements made the "water pinch" method capable of optimizing industrial water networks with streams containing several contaminants. Recent developments showed the method to be capable of handling simultaneous energy and water minimization for water streams containing a single contaminant. Another area of research is based on mathematical programming e.g. linear programming (LP), nonlinear programming (NLP), mixed-integer linear programming (MILP) and mixed-integer nonlinear programming (MINLP). We are going to present the state-of-the-art overview in this two areas (if not covered by someone else) and present our experiences.

In spite of the improvements that can be made to reduce fresh water intakes, using either the "water pinch" approach or any of the approaches based on the mathematical programming, contribution of good water management practice to water usage minimization should not be neglected. Results of our studies, performed on a petrochemical complex and beet sugar plant with the 7 % reduction in fresh water usage in the petrochemical complex and 69 % reduction in fresh water intake in the beet sugar plant indicate that substantial reduction of water usage can be achieved using good housekeeping practice. We are going to present the recent development in this area.

Approaches to minimize industrial water usage

Peter Glavič and Miloš Bogataj

NATO/CCMS Pilot Study on Clean Products and Processes
2006 Annual Meeting

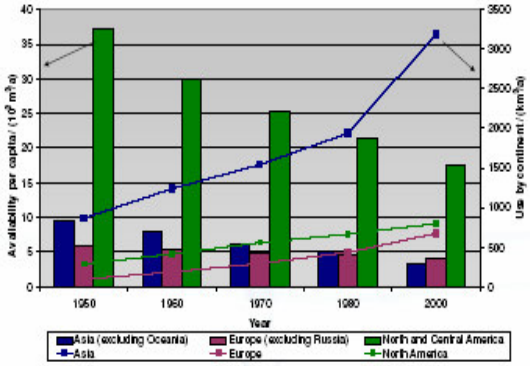
Outline

1. Introduction
2. Why and how to reduce water consumption
   2.1 Good water management practice
   2.2 Conceptual design
   2.3 Mathematical programming
3. Case studides
   3.1 Textiles dyeing mill
   3.2 Rafinery and petrochemical complex
   3.3 Beet sugar plant
4. Conclusions

1. Introduction

- Constant, unsustainable growth of water demand:
  - 20 % of fresh water drawn is currently used by industry
- Diminution of fresh water supplies
  - 33 % reduction of average fresh water supply in the next 20 years
- Unavoidable raise of water costs
- Chemical and process industry is one of the greatest water consumers

Water availability and usage



Source: Rosegrant, 1997

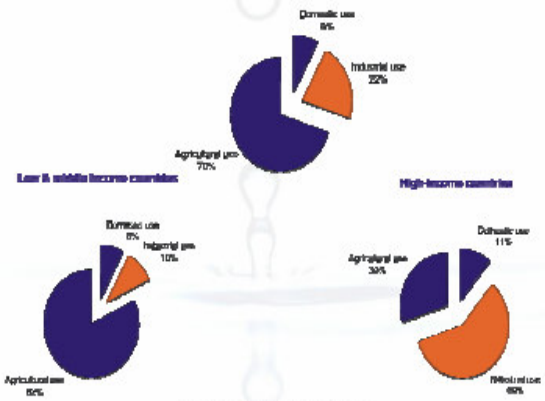


Fig. 1: Competing water users (UNIDO, 2003)

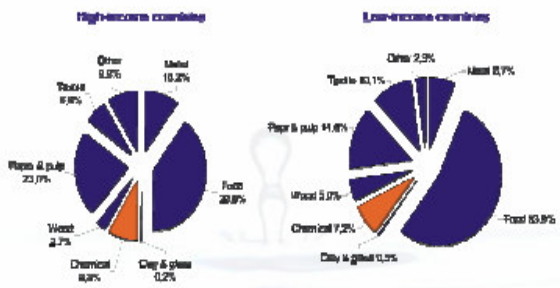


Fig. 2: Contribution of main industrial sectors to production of organic pollutants (UNIDO, 2003)

2. Why and how to reduce consumption

- Beside water scarcity and economic consideration there are several other reasons:
  - discharge permit compliance
  - priority of legislation banning
  - "good neighbour" policy, etc.
- Water usage reduction can be achieved by implementation of solutions obtained by:
  - Good water management practice
  - Conceptual design ('water pinch')
  - Mathematical programming: APs, GAs, LP, NLP, MILP, MINLP

2.1 Good water management practice

- Good water management practice is based on:
  - Collection of process data by constant monitoring
    - Measurements of water and wastewater flow rates
    - Analysis of water and wastewater quality (contamination)
- It is of the outmost importance for retaining status-quo in water consumption
  - e.g. identification and prevention of water leakages

2.2 Conceptual design, "water pinch"

- Graphical targeting method introduced by *Wang and Smith* (1994)
  - based on the use of limiting water profile (plotting cumulative of mass exchanged vs. composition)
- Targets are set ahead of the design
- Capable of handling single or multiple contaminants
- Wastewater consumption can be reduced by:
  - Re-use
    - waste water used directly in other operations
  - Regeneration re-use
    - wastewater is refined and reused in other process
  - Regeneration recycling
    - removal of contaminants and recycling water to the same process

2.3 Illustrative example (*Wang and Smith*, 1994)

- Total site: 4 water using processes
- Single contaminant
- Contaminant inlet – outlet concentration constraints:
  - Minimum mass transfer driving force
  - Maximum solubility
  - Fouling of equipment
  - Corrosion limitations
  - etc.

Tab. 1: Limiting process data.

Process	Mass load of contaminant (kg/h)	c_{in} (ppm)	c_{out} (ppm)	Water flowrate (t/h)
P1	2	0	100	20
P2	5	50	100	100
P3	30	50	800	40
P4	4	400	800	10

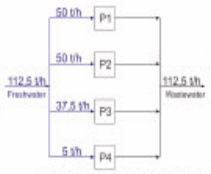
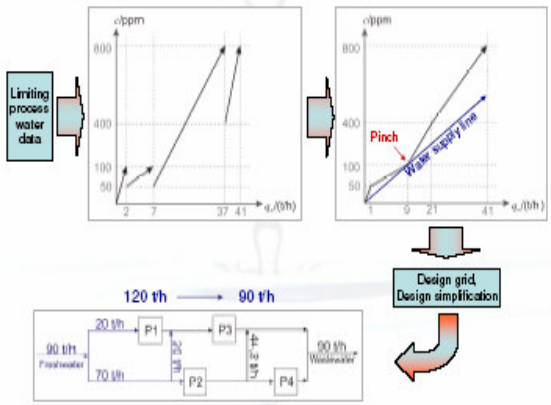
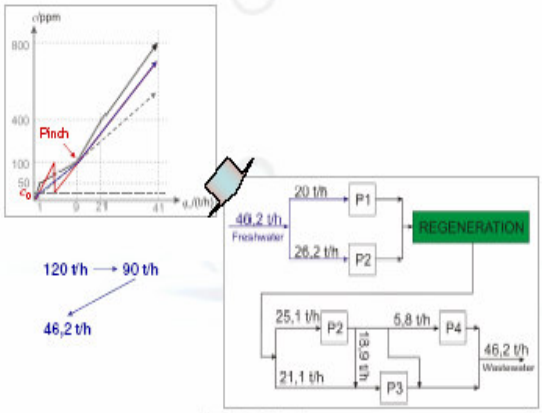


Fig 3: Using freshwater in each process.

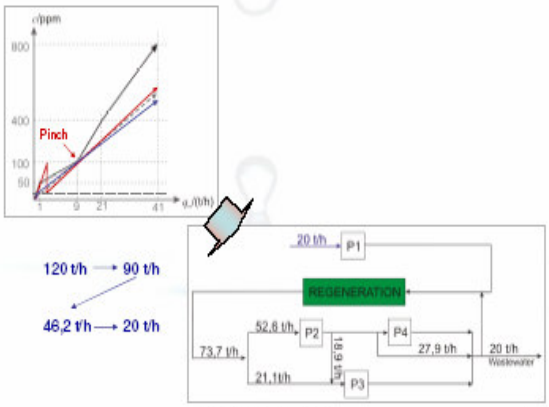
"Water Pinch" – Water re-use



"Water Pinch" – Water regeneration and re-use



'Water Pinch" – Water regeneration and reycle



2.3 Mathematical programming

- Algorithmic procedures
- Genetic algorithms

- Linear programming (LP)
- Nonlinear programming (NLP)
- Mixed-integer linear (MILP)
- Mixed integer nonlinear (MINLP)

} PROGRAMMING

Algorithmic Procedures (APs)

- *Savelski and Bagajewicz* (2000) presented the necessary conditions of optimality in water allocation problems (for processes with a single contaminant)
  - monotonicity of outlet concentrations
  - maximum outlet concentration for head processes (H)
  - maximum outlet concentration for intermediate processes (I)
  - maximum outlet concentration for terminal processes (T)

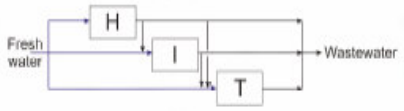


Fig. 4: Shematic representation of water network (*Savelski and Bagajewicz*, 2000)

- Necessary conditions of optimality were employed in the development of NON-ITERATIVE ALGORITHMIC PROCEDURE to design water utilization networks (*Savelski and Bagajewicz*, 2001)
- The procedure always provides:
  - minimum fresh water target
  - real network
- The design can be performed totally by hand even for large-scale processes with <u>single</u> contaminants
- *Savelski and Bagajewicz* (2003) presented the necessary conditions of optimality for water utilization systems in process plants with <u>multiple</u> contaminants
  - algorithmic procedure is under development

Genetic Algorithms (GAs)

- GAs offer a robust non-linear search technique
- Suitable for solving problems with large number of variables
- GA based program developed by *Prakotpol and Srinophakun* (2004) enables:
  - Identification of water reuse and recycle possibilities (single contaminants)
  - Identification of water reuse possibilities (multiple contaminants)
- The hybrid optimization technique based upon GA, presented by *Lavric et al.* (2005) guaranties:
  - Optimal topology of the network
  - Minimum supply water consumption
  - Usage of multiple water sources (fresh or contaminated)

LP, NLP, MILP and MINLP

- *Takama et al.* (1980) introduced nonlinear mathematical programming (NLP) to solve a refinery water distribution network example
- *Savelski and Bagajewicz* (2000) showed that the problem can be linearized for single contaminants (LP)
  - The problem was later formulated as a MILP
- In late nineties several authors presented MINLP models (global optimality is not guarantied)
- Recently *Karrupiah and Grossmann* (2006) presented a global optimization technique – problem was formulated as a non-convex NLP

Summary

- 'Water pinch' – conceptual design
  - Offers understanding and excellent insight to the water network design
- Mathematical programming
  - APs, LP
    - However, "real problems" are nonlinear
    - Simple processes (single contaminant)
    - Limited mainly to mass balances
  - GAs, NLP, MILP, MINLP
    - Offer possibility of simultaneous optimization of mass, energy, and cash flows
    - Profound mathematical knowledge and modeling skils needed

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Outlook

- *Savulescu et al.* (2005) presented study on simultaneous energy and water minimization
  - Single contaminant
- Development of conceptual and mathematical programming methods to enable simultaneous optimization of:
  - energy, water and mass flows with the objective fuction containing
  - environmental, economic and societal impacts

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3. Case studies

3.1 Textile dyeing mill
3.2 Refinery and petrochemical complex
3.2 Sugar beet extraction plant

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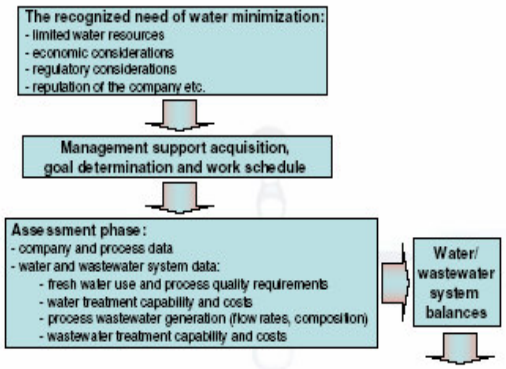
Water minimization strategy



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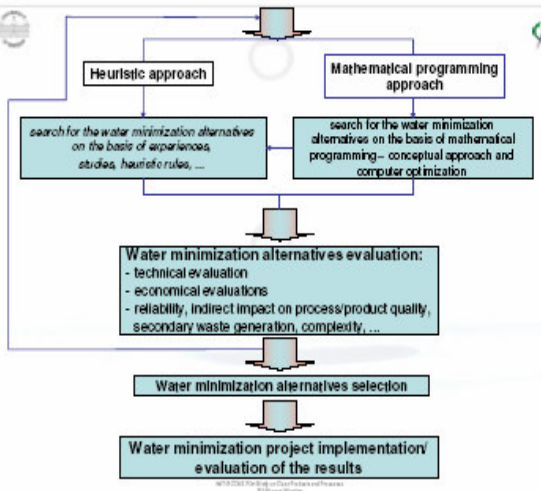

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3.1 Textile dyeing mill

- Good housekeeping and regular maintenance
- Prewashing and afterwashing:
  - shorter in machine dyeing mill
  - no prewashing in piece dyeing mill
- Installation of a new dye kitchen
- Reusing cooling water for dyeing and rinsing
- Reusing condensate for the boiler feed water
  - reusing water blow down for heating buildings
- Reducing steam losses by:
  - changing steam traps, using expanded steam

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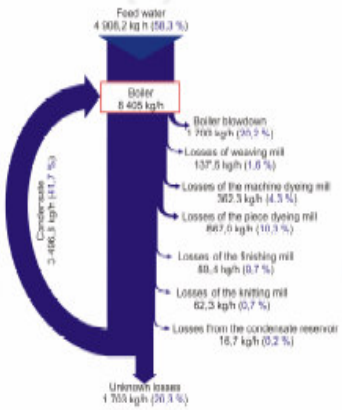
Sankey diagram of steam losses & condensate return



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Results

- Waste water reduction: 153 000 m³/a (21 %)
  - including soft water reduction 78 300 m³/a (15 %)
- Steam reduction: 8 100 m³/a (25 %)
- Dyes reduction: 7 300 kg/a (24 %)
- Other chemicals reduction: 73 800 kg/a (14 %)
- Natural gas reduction: 342 000 m³/a (15 %)
- Economic results of the integral approach:
  - Investment: 67 100 EUR
  - Savings: 237 600 EUR/a
  - Total payback time: 0,25 a

25

3.2 Refinery and petrochemical complex

- Petrochemical activities in the company
  - Formaldehyde production (two lines)
    - Wastewater reused in stripper column, but 2,3 m³/h into sewer
  - Synthetic (urea- and phenol-formaldehyde) resin production
    - Surface water is used for vacuum pumps (16,9 m³/h)
    - Potable and cooling water for other users (2,3 m³/h)
  - Methanol production (Lurgi process)
    - Cooling water is used for cooling samples and condensate
    - All cooling water ends as wastewater (6,5 m³/h)
- Refinery
  - Atmospheric distillation
    - Out of 9,2 m³/h wastewater produced, 2,2 m³/h unpolluted

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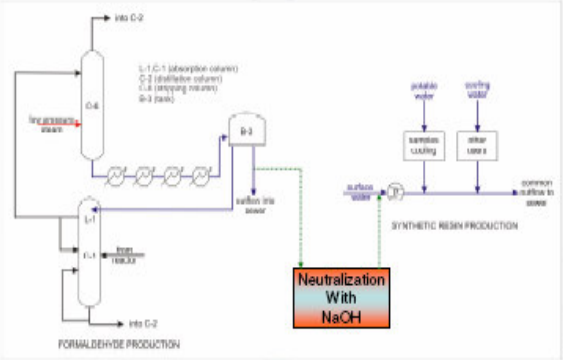

Fig. 6: Water flow diagram in formaldehyde and synthetic resin production

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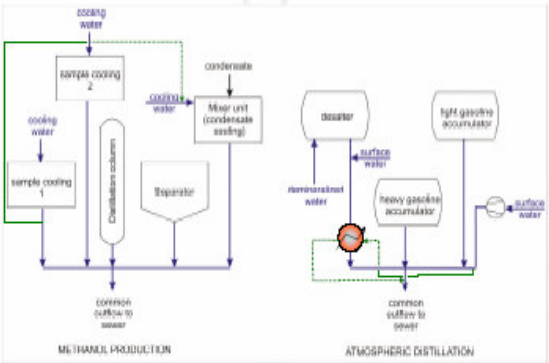

Fig. 7: Water flow diagram in methanol production and synthetic atmospheric distillation

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Proposed water minimization options

- Wastewater regenerated and reused in site: formaldehyde production → synthetic resin production, regeneration using neutralization with alkali
- Cooling water reused in sample coolers & mixer (within the methanol plant)
- Cooling water from pump outlets reused for cooling the desalter outflow from 125 ºC → 32 ºC
- Total savings: 11,2 m³/h or 80 700 m³/a

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Results

- Total site integration of water was applied
- Petrochemical complex proposals:
  - 24 % reduction in total volume of water used
  - Total savings → 27 600 EUR/a
  - Payback time: 6 months
- Refinery proposals:
  - 14 % reduction in total volume of water used
  - Total savings → 15 500 EUR/a
  - Payback period: 11 days
- Water tax has doubled the savings next year

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3.3 Beet sugar plant

- Sugar industry is one of the major water consumers and wastewater producers, e.g. Slovenian company *TSO* is:
- Processing 4 200 t/d of sugar beets:
  - fresh water required 2 000 t/d
  - wastewater discharged 4 600 t/d (sugar beet contains 76 % water)
- Tendency in sugar plants today is "zero" water consumption, excluding water for the boiling house
- The study was aimed to reduce fresh water usage, consequently reducing wastewater production

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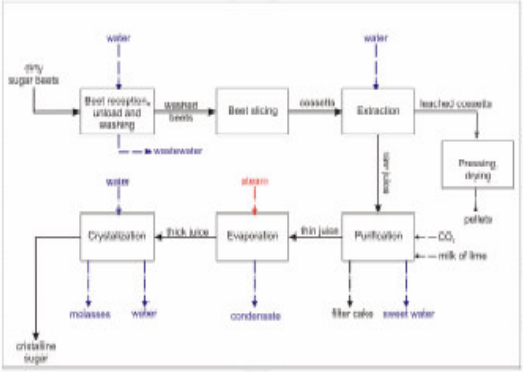

Fig. 8: Process flow diagram of sugar manufacturing process

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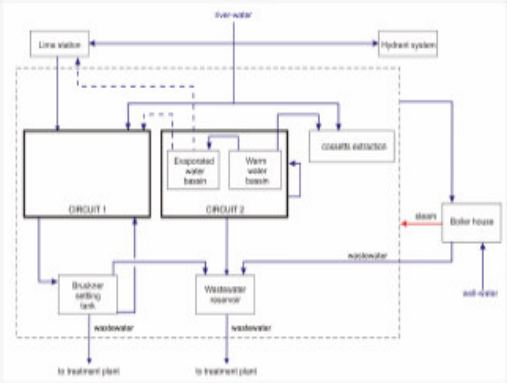

Fig. 9: Simplified water/wastewater system in sugar manufacturing process

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Proposed water minimization options

- Water in the evaporated water basin disinfected,
  - and reused in the lime station and circuit I
- Condensate from evaporation stage recovered,
  - and used as feed water for boiler
- Irruptive water flow into the flume system limited,
  - thereby reducing expenses for water tax
- River water stream replaced with
  - water from warm water basin
- Total savings: 108 m^3/h or 216 000 m^3/a

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Results

- Beet sugar plant proposals:
  - 69 % reduction in total volume of water used
  - Total savings per season (83 days) → 42 500 EUR
  - Payback time: 5 days
- "Zero waste" concept introduced for
  - water
  - solids (sliced beet, sulphate)
  - gaseous emissions
- Biorefinery
  - bioethanol
  - organic specialty products

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WATER MANAGEMENT AND REDUCTION OF DIOXIN EMISSIONS IN THE STEEL INDUSTRY IN FLANDERS

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Abstract

Companies more and more adapt their process according to the principles of cleaner production: minimal use of (non-renewable) energy, minimal use of (non-renewable) resources and minimal production of waste.

Different measures can be taken to decrease the impact of a process on the environment: good housekeeping, input change, technical modification in an existing process, developing of a new process, process intensification and industrial ecology. These measures are illustrated using examples from different sectors. Particular attention will be given to applications of industrial ecology in the steel and chemical industry in Flanders.

Water management and reduction of dioxin emissions in the steel industry in Flanders

C. Block, Leuven Engineering School Groep T
C. Vandecasteele, Dept. of Chemical Engineering K.U.Leuven
R. Mortier, Sidmar, Ghent
Istanbul
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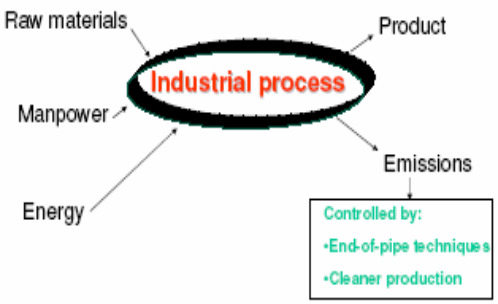
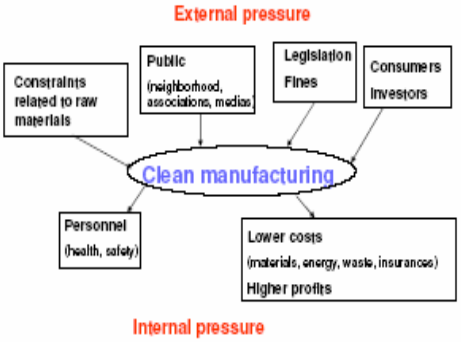
1. Industrial process



2. Cleaner production: pressures



Cleaner production: objectives

- Raw matererials, auxiliaries, water
  - Minimal use, especially for non-renewable
  - Recycling of waste, water and by-products
- Energy
  - Minimal use, especially of non-renewable
  - Recycling
- Minimal production of (toxic) waste
- Minimal emissions to air, water and soil

3. Sidmar: steel production

- Sidmar is part of the Arcelor-group
- 2nd large steel production company in the world
- Industrial park Ghent (canal area)
- 2004: 6 10^6 ton iron ore ⇒ 4.6 10^6 ton products
- Problems
  - Sinter plant: dioxin emissions
  - Energy intensive process: huge use of cooling water and process water

3.1. Steel production

- Handling of raw materials
  - Iron ore, fluxes, coke
- Coke production
  - Energy supplier and reductans in blast furnaces
- Blast furnaces
  - Sinter pellets (iron ore and fluxes) ⇒ pig iron
- Steel plant
  - Refining of pig iron by reduction of impurities
- Hot rolling and cold rolling mills
  - Liquid steel ⇒ billets, blooms, slabs…⇒ finished products

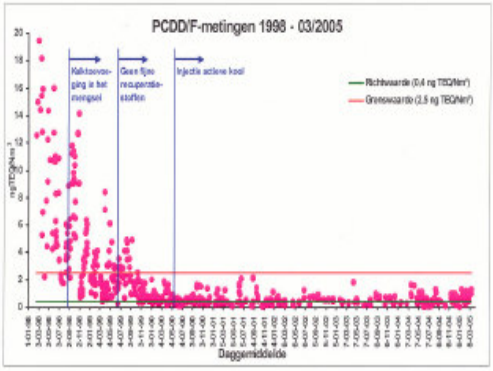
3.2. Dioxin emissions of sinter plants

- 1997: dioxin emissions of 20 ng TEQ/Nm³
  - Flemish Environmental Agency asked to reduce emissions < 0,5 ng TEQ/Nm³ before 1999
  - 1999: Vlarem (Flemish legislation)
    - sinter plants
      - Emission standard: 2,5 ng TEQ/Nm³
      - Emission target value: 0,4 ng TEQ/Nm³

Dioxin emissions of the sinter plant

- Solving problem by combination of
  - Process integrated measures
    - Chemical composition of sinter pellets
      - Flux: use of CaO instead of $CaCO_3$ ⇒ improved permeability of sinter mixture
      - Elimination of recycled material with particles < 10 µm (used in sinter mixture)
  - End-of-pipe techniques
    - Injection of activated carbon + multicyclone and electrofilter

Dioxin emissions of the sinter plant

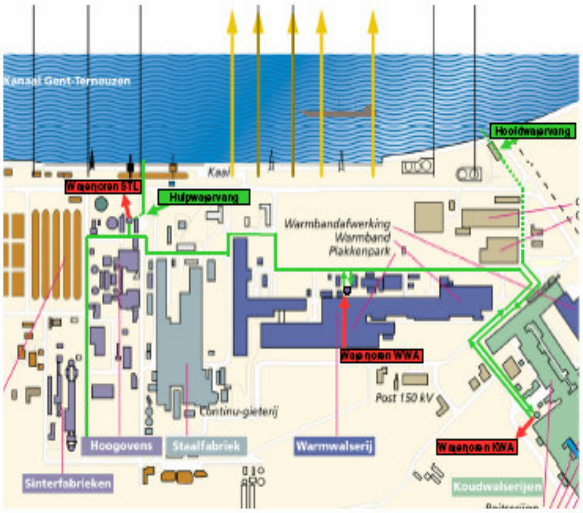


3.3. Sustainable water management

- Steel industry is energy intensive
  - Cooling water for several processes, environmental technical and sanitary applications
  - Canal water, ground water, drinking water
  - 1993: 430 10^6 m³ water use ⇒ 43 10^6 m³ canal water pumped: recycling level of 10
  - 1993-1998
    - Improving performance of existing water infrastructure
    - Decreasing of water use

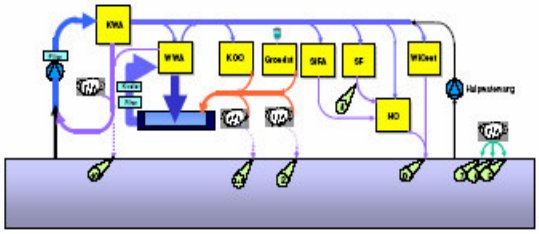
Sustainable water management

- Judicious implantation of production units with minimal internal transport of water
- Projects water management
  - Water recycling
  - Demineralisation of canal water using reverse osmosis
  - Biological treatment of waste water from coke plant
  - Neutralisation of waste water from blast furnaces with alkaline water from the steel plant (industrial symbiose)
- Several Environmental Awards from VBO (organisation of Belgian companies)



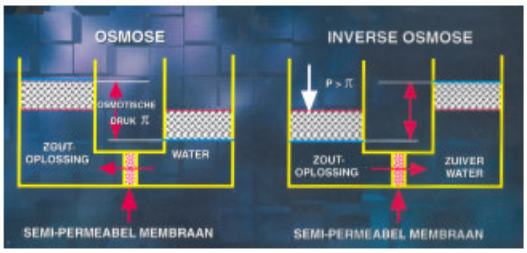
a. Water recycling

Past: 700-800 m³/h discharged via 10. **Now** pumped up via main water supply. In hot rolling mill circulation of 14000 m³/h. At the moment suppletion of only 1000 m³/h



KWA=cold rolling mill; WWA=hot rolling mill; KOO=cokes plant; grondst= raw materials; SIFA=sinter plant; SF=steel plant; HO= blast furnaces; WKcent=wind power station

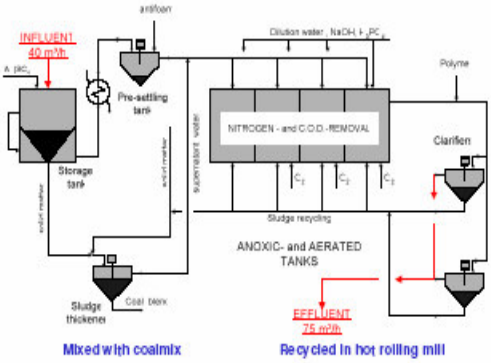
Principle of reverse osmosis



b. Demineralisation of canal water

- Reverse osmosis
  - 4 installations
  - Total capacity:
    ⇒ 430 m³/h
  - Use of artesian well discontinued
    ⇒ protection of ground water

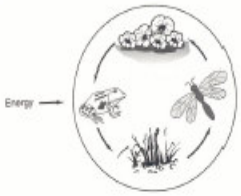
c. Biological treating of waste water from cokes plant



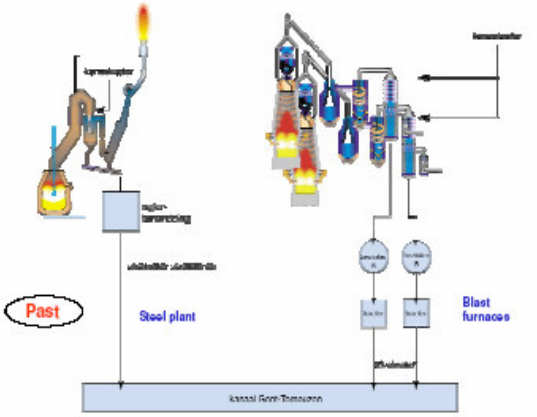
Parameter	Influent	Effluent	Efficiency
Flowrate (m³/h)	40	75	
COD (mg/l)	3250	205	93.6
BOD (mg/l)	1720	11.3	99.3
Ammonia N (mg/l)	153	3.2	97.9
SCN^- (mg/l)	465	0.3	99.9
Sulfates (mg/l)	-	772	
Sulfites (mg/l)	16	0.18	98.9
Phenols (mg/l)	550	0.025	99.9
Susp. Solids (mg/l)	60.5	64	

Industrial symbiosis

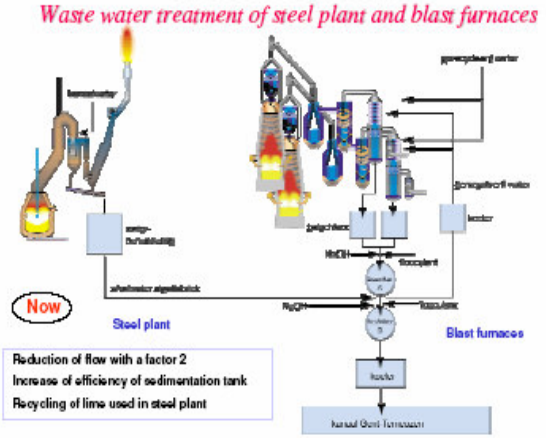
- Industrial symbiosis or industrial ecology
  - Inspired on ecological systems
  - Approach for the optimisation of use of raw materials, energy and capital
  - Base concept: *making material* and *energy flows cyclical*
  - Symbiosis between different companies or parts of large industrial complexes



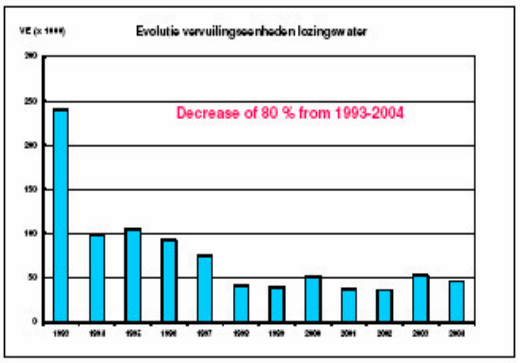
d. Waste water treatment steel plant and blast furnaces



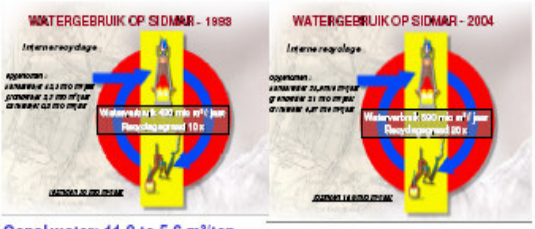
INDUSTRIAL symbiosis:
Waste water treatment of steel plant and blast furnaces



Evolution of discharges of waste water: pollution units



Water management



Canal water: 11.8 to 5.6 m³/ton

Canal water: - 16.4 10^6 m³/y

Discharges: - 13.2 10^6 m³/y

Recycling level: x 20

Production: + 28 %

EVALUATION OF SEVERAL ZEOLITES AS SULFUR COMPOUNDS ADSORBENTS BY INVERSE GAS CHROMATOGRAPHY

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Abstract

Desulfurization of transportation fuels (gasoline, jet fuel and diesel fuel) has become an important issue because of their increasing demand and environmental impact. Zeolites have been used in catalysis and adsorption processes to lower the sulphur content in the final product. In this work, Inverse Gas Chromatography (IGC) has been explored to study the adsorption capacity and selectivity of different adsorbents for some sulphur compounds. Results of the systematic study of the adsorption properties of sulphur compounds over zeolites are used to explain the behaviour of these materials as adsorbents for ultra-deep desulphurization of fuels. The S-compounds chosen as model compounds are thiophene and 2,5-dimethylthiophene, whereas NaX, HX, NaY and HY zeolites are chosen as adsorbents. Among the zeolites studied, NaY showed the highest adsorption capacity. Adsorption isotherms in gas phase are not representative of saturation adsorption in the liquid phase. However, the heat of adsorption and the specific interaction parameter give comparable data of the strength and the selectivity of S-compounds adsorption over different adsorbents in liquid phase. The main conclusion of this work is that IGC is a useful tool for preliminary selection of adsorbents to remove S-compounds from fuels.

UNIVERSITY OF OVIEDO, Spain

NATO/CCMS Clean Products and Processes
Istanbul (Turkey) May 8-12, 2006

DEPARTMENT OF CHEMICAL ENGINEERING AND ENVIRONMENTAL TECHNOLOGY

EVALUATION OF SEVERAL ZEOLITES AS SULFUR COMPOUNDS ADSORBENTS BY INVERSE GAS CHROMATOGRAPHY (IGC)

Eva Díaz
Salvador Ordóñez
Aurelio Vega
José Coca

INTRODUCTION

- Removal of sulfur compounds in fuels:
  - Environmental pollution: acid rain
  - Poisoning of catalytic converter for exhaust emission treatment
- Sulfur content regulations:
  - Europe
    - Both fuels (2005): 50 ppmw
  - USA (Environmental Protection Agency)
    - Gasoline (2006), from 300 to 30 ppmw
    - Diesel (2006), from 500 to 15 ppmw
    - 2009: 10 ppmw

TECHNIQUES OF DESULFURIZATION

- Hydrotreatment
  - Reduction of octane number
- Gas scrubbing
- Membranes
- Absorption
- Distillation

} low selectivity and/or energy intensive problems

- Selective adsorption: potential technique

TECHNIQUES OF DESULFURIZATION

PROCESS	PROCESS CONDITIONS	COMMENTS	COMMERCIAL TECHNOLOGY
Reactive adsorption	370-420ºC, 34bar	Removes sulfur by using reduced metals or metal oxides to react with sulfur to form metal sulfides at elevated temperatures under H_2 atmosphere without hydrogenation of aromatics	ConocoPhillips
Selective adsorption	Ambient temperature, ambient pressure	The adsorbent can selectively adsorb the sulfur compound	Black & Veatch Pritchard Incorporation; Alcoa Industrial Chemicals
Oxidation	30-70ºC, ambient pressure	Produces oxidized compounds that can be physically separated and could be easily processed downstream	Petrostar
Extraction	Low temperature and low pressure	It is based on the fact that organosulfur compounds are more soluble than hydrocarbons in an appropriate solvent	GT-DeSulfUR process
Pervaporation	30-70ºC, <1bar	Separation is affected by the preferential sorption of S of the feed liquid by the membrane, diffusion species into low pressure permeate stream	Dupont
Biodesulfurization		Removes sulfur from fossil fuels using a series of enzyme-catalyzed reactions	Energy BioSystems
Hydrodesulfurization	300-400ºC, 30-4bar	Middle distillate hydrogenation from the FCC	Akzo Nobel

REVIEW OF ADSORPTION STUDIES

- Adsorbents
  - Activated carbons
  - Red mud
  - Alumina
  - Zeolites (NaX, CaA, NaY)
- Techniques
  - Fixed bed
  - Static volumetric method
  - Thermobalance
  - Flow microcalorimetry in liquid phase
  - Inverse gas chromatography (IGC)

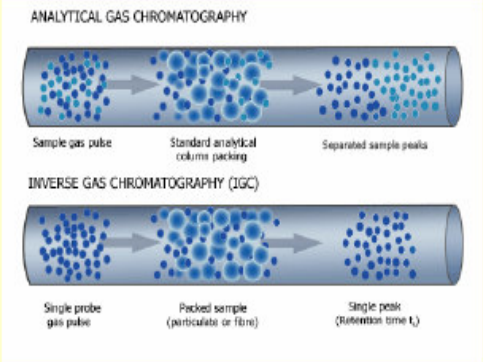
OBJECTIVES

Determination of the adsorption capacity of different zeolites (NaX, HX, NaY, HY) and thermodynamic parameters by IGC

Adsorbates: thiophene, 2,5-dimethylthiophene, alkanes, benzene

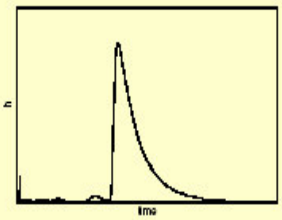
- Disadvantages of conventional techniques (equilibrium techniques):
  - time-consuming
  - extreme conditions (vacuum)
- Advantages of dynamic techniques (ex. IGC):
  - fast
  - ambient P in a wide range of T

INVERSE GAS CHROMATOGRAPHY



INVERSE GAS CHROMATOGRAPHY

CHROMATOGRAM



SPECIFIC RETENTION VOLUME

$$V_g = Fj\frac{(t_R - t_M)}{m}\left(\frac{p_0 - p_w}{p_0}\right)\left(\frac{T}{T_{meter}}\right)$$

ENTHALPY OF ADSORPTION

$$\Delta H_{ads} = -R\frac{\partial(\ln V_g)}{\partial(1/T)}$$

INVERSE GAS CHROMATOGRAPHY
Surface Properties

- Free energy of adsorption

$$\Delta G_{ads} = -RT\ln\left[\frac{P_1 V_N}{\pi_0 Sm}\right]$$

- Free energy of adsorption is related to the Work of adhesion, W_a, between a molecule and a solid. This Work of adhesion is due to:
  - Dispersive interactions
  - Specific interactions (acid-base)

INVERSE GAS CHROMATOGRAPHY
Surface Properties

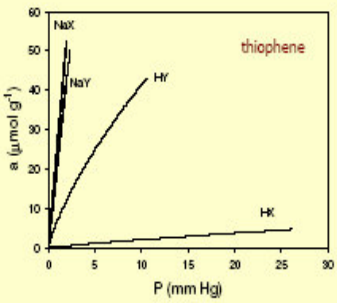
- Dispersive component of surface energy

$$\gamma_S^D = \frac{1}{4}\frac{\Delta G_{CH_2}^2}{\gamma_{CH_2} N^2 a_{CH_2}^2} \quad \text{where} \quad \begin{cases} \Delta G_{CH_2} = -RT\ln\dfrac{V_{N(n)}}{V_{N(n+1)}} \\ \gamma_{CH_2} = 35.6 + 0.058(20 - T) \end{cases}$$

- Specific component of surface energy

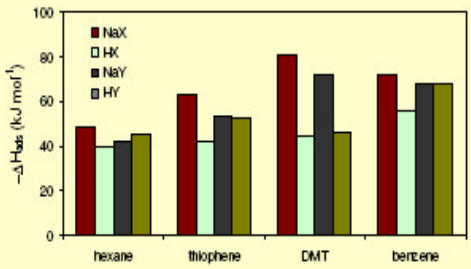
$$I^{sp} = \frac{\Delta(\Delta G)}{Na}$$

INVERSE GAS CHROMATOGRAPHY
Capacity of adsorption

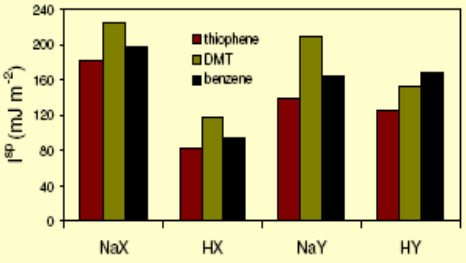


DMT > thiophene > benzene > *n*-hexane

INVERSE GAS CHROMATOGRAPHY
Enthalpy of adsorption



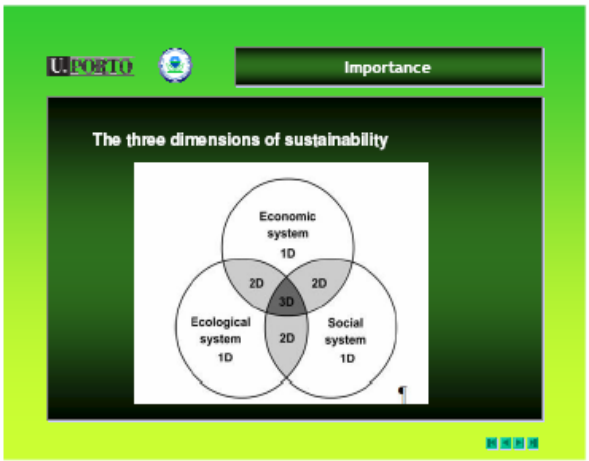
INVERSE GAS CHROMATOGRAPHY
Specificity of interaction

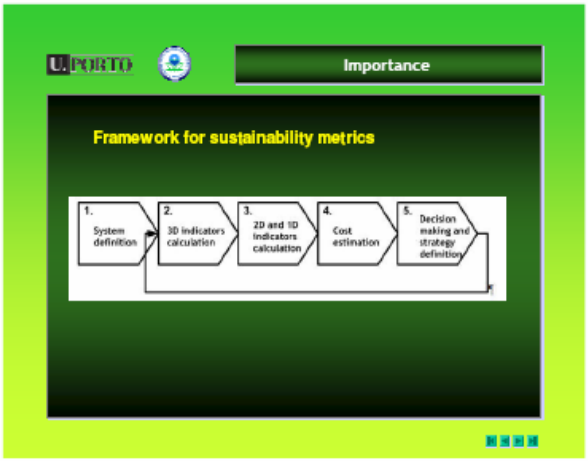


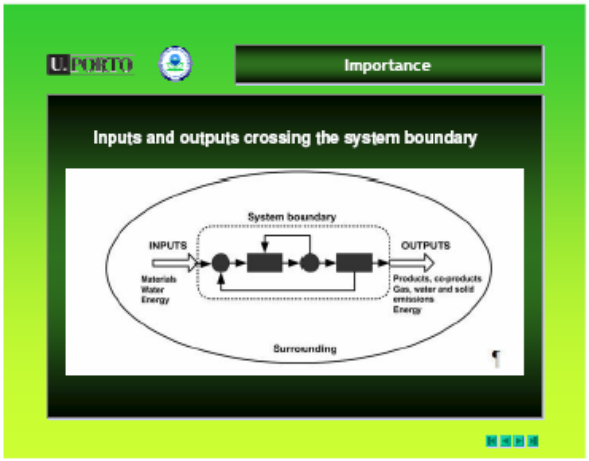
CONCLUSIONS

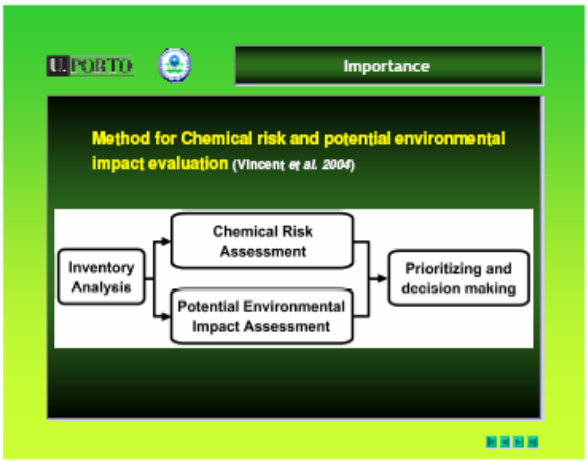
- Enthalpies of adsorption obtained by IGC are a good indication of the performance in liquid phase
- A good indication of the specificity of the adsorbent-adsorbate interaction can be obtained by IGC

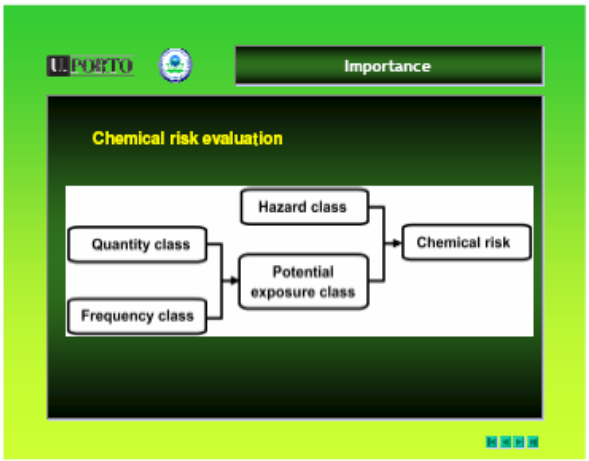
OPEN DISCUSSION ON METRICS FOR SUSTAINABLE TECHNOLOGIES (Moderated by Dr. Subhas Sikdar)











Importance

"Quantity class"

expressed as the ratio of the quantity of each chemical i to the quantity of the most used chemical in the process, q_{max}. This way, five levels of "quantity class" are defined:

- level 1 for $q_i/q_{max} \leq 1\%$
- level 2 for $1\% < q_i/q_{max} \leq 5\%$
- level 3 for $5\% < q_i/q_{max} \leq 12\%$
- level 4 for $12\% < q_i/q_{max} \leq 33\%$
- level 5 for $q_i/q_{max} > 33\%$

Importance

"Frequency class"

Use	Occasional	Intermittent	Frequent	Permanent
Day	< 30 minutes	30 – 120 minutes	2 – 6 hours	> 6 hours
Week	< 2 hours	2 – 8 hours	1 – 3 days	> 3 days
Month	< 1 day	1 – 6 days	6 – 15 days	> 15 days
Year	< 5 days	15 days– 2 months	2 – 5 months	> 5 months
Class	1	2	3	4
	Interrupted, 0 , when the use of the chemical agent has been interrupted during more than one year or definitively			

Importance

"Hazard class"

Hazard class	Risk phrases and combinations	Pictogram	TLV (mg/m3)	Type of chemical agent
1	None	None	>100	
2	R26, R27, R28, R26/27, R26/28, R26/27/28, R33/38 R60		[0,100]	Asia / cereals / Graphite / Construction materials / Talc / Cement / Composite materials / Combustion of fossils/fuels / Solder / Plastic metals / Values (silver / Vegetables - minerals)
3	R20, R21, R22 R20/21, R20/22, R20/21/22, R11/22 R23, R24, R40 R42, R43, R42/43 R48/20, R48/21, R48/22, R48/20/21, R48/20/22, R48/21/22 R48/20/21/22 R48/20/22, R48/20/21/22 R60, R63, R64, R68, R67, R68		[..,10]	Uncoordinable solder / Ceramic fibers - vegetables / Paints with plumb / sand / lubricant oils
4	R10,R39 R23, R24, R25, R26, R33, R33/34, R33/35, R33/34/35, R35, R36/37, R36/38, R36/37/38, R36/38/39, R36/38/40, R36/38/40/41, R36/38/41/55 R41, R48, R48, R48, R48, R48/23, R48/24, R48/25, R48/23/24, R48/23/25, R48/24/25, R48/23/24/25 R60, R61		[0.1,1]	Wood and derivates / Plumb / Asbestos / Plumb melting / Tins / Mercury Gasoline (fuels) / ...
5	R26, R27, R28, R32 R26/27, R26/28, R26/27/28, R27/28, R39, R39/26, R39/27, R39/28, R39/26/27, R39/26/28, R39/27/28, T39/39/40		<0,1	

Importance

"Potential exposure class"

Quantity class \ Frequency class	0	1	2	3	4
5	0	4	5	5	5
4	0	3	4	4	5
3	0	3	3	3	4
2	0	2	2	2	2
1	0	1	1	1	1

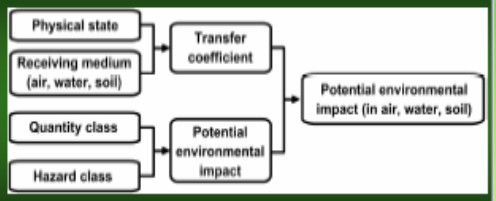
Importance

"Chemical Risk Determination"

Hazard class \ Potential exposure class	1	2	3	4	5
5	100	1 000	1 000	100 000	1 000 000
4	30	300	3 000	30 000	300 000
3	10	100	1 000	10 000	100 000
2	3	30	300	3 000	30 000
1	1	10	100	1 000	10 000

Importance

Potential Environmental Impact evaluation



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Importance

"Hazard Class"

Hazard class	Risk phrases and combinations
1	Note The residue type is not mentioned on the residue classification list. Not danger industrial residue
2	R66, R67 The type of residue is mentioned (with an asterisk) in the residues classification. R29 and accidental probability of a contact with water R31 and accidental probability of a contact with acid
3	R20, R21, R22, R33, R36, R37, R38 R4(R20), R4(R21), R4(R22), R4(R20/21/22), R4(R28), R4(R21), R4(R22) R4(R20/21), R4(R20/22), R4(R21/22), R4(R20/21/22) R32, R33, R1(R33), R65 R29 and R32 and accidental probability of a contact with water R31 and accidental probability of a contact with acid
4	R23, R24, R25, R34, R35, R40, R41, R42, R43, R48 R4(R23), R4(R24), R4(R25), R4(R23/24), R4(R23/25), R4(R24/25) R4(R23/24/25), R50, R51/53, R34, R35, R36, R37, R38, R39 R62, R63, R64 R29 and permanent probability of a contact with water R31 and permanent probability of a contact with acid R32 and occasional probability of a contact with acid
5	R26, R27, R28 R1(R25), R1(R24), R1(R23), R1(R23/24), R1(R23/25), R1(R23/24/25), R1(R26), R1(R27), R1(R28) R1(R26/27), R1(R26/28), R1(R27/28), R1(R26/27/28) R45, R46, R49 R50, R51/53 R60, R61 The type of residue is mentioned (with an asterisk) in the residues classification. R32 and permanent probability of a contact with acid

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Importance

quantity thresholds

Hazard class	Category	Threshold (kg)
5, 4 , 3	Product, substance, or preparation	5
2, 1		100
5	Residue	100
2, 1		500

U.PORTO

Importance

"Potential environmental impact"

Danger class \ Quantity class	1	2	3	4	5
5	2 000	5 000	10 000	30 000	100 000
4	100	1 000	2 000	5 000	10 000
3	10	30	100	1 000	2 000
2	2	5	10	30	100
1	1	1	2	5	10

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Importance

Transfer coefficients

Physical state \ Receiving medium	Air	Water	Soil
Gas	0,95	0,05	0,001
Liquid	0, 5	0,35	0,002
Solid	0,001	0,005	0,005
Solid as powder	0,1	0,85	0,005

U.S. EPA'S GUIDELINES FOR WATER REUSE

Daniel J. Murray, Jr., P.E.

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Abstract

In August 2004, the U.S. Environmental Protection Agency and the U.S. Agency for International Development published "Guidelines for Water Reuse", updating their 1992 guidelines document. Because communities around the world are reaching, or have reached, the limits of available water supplies, water reclamation and reuse are becoming necessary for conserving and stretching available water resources. Increasing urbanization and its accompanying demands for domestic, industrial, commercial and agricultural water usage, is making the situation worse, especially in water-scarce regions.

This updated guidelines document covers water reclamation for nonpotable urban, industrial, commercial and agricultural reuse and the augmentation of potable water supplies through indirect reuse. Because direct potable reuse is not practiced in the United States, it is only briefly addressed in this document.

This updated guidelines document expands on the coverage of many important issues, including industrial reuse; reuse practices outside of the U.S., and health concerns due to emerging chemicals and pathogens.

The updated guidelines document is structured by topic, addressing types of reuse applications; technical issues in planning water reuse systems; water reuse regulations and guidelines in the U.S.; legal and institutional issues; funding water reuse systems; public involvement programs; and water reuse outside of the U.S.

This updated guidelines document is available from U.S. EPA and can be downloaded or ordered at www.epa.gov/ttbnrmrl.

U.S. EPA's Water Reuse Guidelines

Daniel J. Murray, Jr., P.E.
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U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Cincinnati, Ohio

- History of Guidelines in the U.S.
- Background on Water Reuse
- Overview of Guidelines
  - Water reuse applications
- Overview of Chapters
- How to order and download

History

- Original guidelines published in 1980
- First updated in 1992
- Current guidelines completed in 2004 by U.S. EPA and USAID
- Latest guidelines build on substantial R&D and extensive demonstration projects on water reuse practices around the world
- Major organizations involved include AWWA, WEF, WateReuse Association, NRC/NAS

Background

- World's urban population is expected to increase from about 3 billion to 5 billion over the next 25 years
- Many cities are reaching the limits of their available water supplies
- Water reclamation and reuse are now almost becoming necessary to conserve and extend available water resources
- Reuse of wastewater can also divert discharges away from sensitive aquatic and marine environments

Objectives

- To support municipal water utilities and regulatory agencies in making wise decisions on reuse of treated domestic wastewater
- Addresses water reuse for nonpotable uses in urban, industrial and agricultural settings and augmentation of potable water supplies through indirect reuse
- Direct potable reuse is briefly addressed

Water Quality and Treatment

- Nonpotable water reuse usually requires conventional treatment technologies
- Overriding factor is water quality needed for intended reuse
- Potential for direct human exposure to reclaimed water will likely require higher treatment
- Typically, secondary treatment of domestic wastewater will require filtration and enhanced disinfection before reuse

Urban Reuse Applications

- Irrigation of residential and commercial properties and public parks
- Commercial uses such as vehicle washing, window washing, and mixing water (i.e., concrete production)
- Fountains, reflecting pools, waterfalls
- Dust control
- Fire control
- Toilet flushing in commercial/industrial buildings

Reliability for Public Health Protection

- Urban reuse systems usually require dual distribution systems
- Design safeguards include:
  - Water will meet the quality and quantity requirements of users
  - Insure proper operation of the system
  - Prevention of cross-connections with potable water lines
  - Prevention of improper use of nonpotable water

Industrial Reuse

- Industrial reuse primarily falls into three major categories:
  - Cooling water
    - Once-through systems
    - Recirculating evaporative systems
  - Boiler make-up water
  - Process water

Reuse for Cooling Water

- Once-through cooling
  - Single pass through heat exchangers
  - Few systems use reclaimed water
  - Used where treated effluents are convenient to access and use
    - Bethlehem Steel in Baltimore, Maryland uses 100 mgd (4380 l/s) of treated domestic wastewater from the City of Baltimore treatment plant

Reuse for Cooling Water

- Recirculating evaporative cooling
  - Cooling towers and spray ponds
  - Water quality concerns include corrosion, biological growth and scaling
  - Chemical addition, softening, filtration and chlorination may be required

Reuse for Boiler Make-up Water

- Extensive treatment of reclaimed water needed
- Hardness close to zero
- Calcium, magnesium, silica, alumina removed to prevent scaling
- Lime treatment, multi-media filtration, carbon adsorption, nitrogen removal, reverse osmosis, ion exchange may be necessary
- Several oil refineries in Southern California use reclaimed water as primary source of boiler make-up water

Reuse for Industrial Process Water

- Water quality requirements drive the applicability of using reclaimed water in industrial processes
- Textiles, leather tanning, pulp and paper, metal fabricating have low to intermediate water quality requirements
- Even industries requiring very high quality water can use reclaimed water
  - Full-scale demonstration plant (Toppan Electronics – San Diego) has shown reclaimed water can be used with pretreatment and microfiltration

Reuse in Pulp and Paper

- About a dozen pulp and paper mills use reclaimed water
- Tertiary treatment usually required
- Driven by insufficient sources of fresh water
- Mills not using reclaimed water cite:
  - Concerns about pathogens
  - Product requirements preclude using reclaimed water
  - Prohibitive conveyance costs
  - Concerns about potential corrosion, scaling, and biofouling due to high degree of internal recycling

Agricultural Reuse

- Agriculture is a prime candidate for water reuse
  - Extremely high demands for irrigation
    - 40% of total water demand in U.S.
  - Significant water conservation benefits
    - 48% of reclaimed water in California used for agricultural irrigation
  - Can integrate agricultural reuse with other reuse applications

Environmental and Recreational Reuse

- Environmental Reuse
  - Wetland enhancement/restoration
  - Wetland/habitat creation
  - Stream augmentation
- Recreational Reuse
  - Impoundments
    - Golf course ponds
    - Water-based recreation impoundments
      - Incidental contact
      - Full body contact

Groundwater Recharge

- Purpose
  - Establish saltwater intrusion barriers
  - Provide further treatment for future use
  - Augment potable/nonpotable aquifers
  - Provide storage for reclaimed water for future retrieval and reuse
  - Control/prevent ground subsidence

Groundwater Recharge

- Methods
  - Surface spreading
    - Infiltration and percolation through the soil matrix
  - Soil-aquifer treatment systems
  - Vadose zone injection
  - Direct injection

Augmentation of Potable Supplies

- Surface water augmentation for indirect potable reuse
- Groundwater Recharge for indirect potable reuse
- Direct potable reuse
  - Used by only one city – Windhoek, Namibia
  - Public reluctance to accept direct reuse

Guidelines Summary

- Chapter 2 – Types of Reuse Applications
- Chapter 3 – Technical Issues in Planning Water Reuse Systems
- Chapter 4 – Water Reuse Regulations and Guidelines in the U.S.
- Chapter 5 – Legal and Institutional Issues
- Chapter 6 – Funding Water Reuse Systems
- Chapter 7 – Public Involvement Systems
- Chapter 8 – Water Reuse Outside the U.S.

To order or download go to:

www.epa.gov/ttbnrmrl

"2004 Guidelines for Water Reuse"
Report Number: EPA/625/R-04/108

MEMBRANE ENINEERING IN WATER REUSE AND RECYCLE

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Abstract

Membrane engineering made significant progresses in recent years, particularly in the areas of sea water and brackish water desalination and water treatments in general.

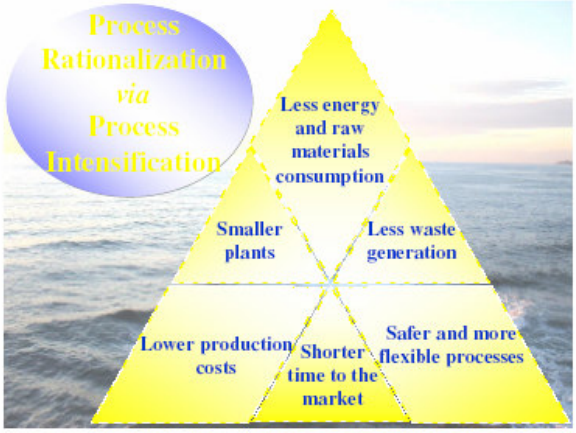
Integrated membrane operations have been realized well consistent with the processes intensification strategy, and able to contribute to important reductions in energy consumption, minimizing also environmental impacts.

The development of new membrane operations as the membrane contactors and the production of new membrane, operating at high temperature and also in non-acqueous systems, might contribute to further applications of these technologies such as the ones in the petrochemical industry.

Membrane Technology for Seawater/ Brackish Water Desalination and Municipal Wastewater Treatment

Enrico Drioli, Francesca Macedonio

Research Institute on Membrane Technology (ITM-CNR)
c/o Department of Chemical Engineering and Materials, University of Calabria - Arcavacata di Rende, Italy
www.itm.cnr.it



Membrane Technology

- High efficiency and operational simplicity
- High selectivity and compatibility
- Low energy and chemicals consumption
- Good stability and modularity
- Easy control and scale-up

The membrane industry is an important economic factor

Global membrane market state 2002:
US$ 4.5×10^9 (ICOM 2002, Toulouse, France)

Global membrane market state 2004:
US$ 8.46×10^9 (Euromembrane 2004, Hamburg, Germany)

Growing interest towards membrane science and technology is evident:

✓At the 9th World Filtration Congress (New Orleans, USA) most of the scientific communications concerned applications of membrane systems in various production sectors.

✓About 200 exhibitors connected with the membrane world at the 9th edition of ACHEMA (Frankfurt, Germany)

✓Numerous research projects on the field of membrane science and technology, approved, in progress or carried out in the latest years, with the financial support from the European Union.
In particular, a Network of Excellence: "Expanding membrane macroscale applications by exploring nanoscale material properties (NanoMemPro)", has been recently approved in the 6th Framework Programme (2002-2006) of the EU, and is now in progress

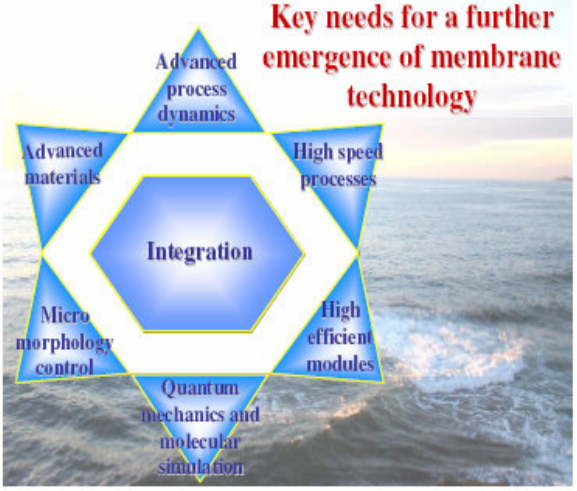
Significant transformations in the European membrane industry are also confirming the maturity of the membrane operation in various industrial areas:

✓DSS acquisition by Alfa Laval (2002)

✓Nadir and Microdyn merging in the Advanced Separation Technologies Group Membranes (2003)

✓Osmonics, Ionics (2005) and ZENON (March 2006) acquisition by General Electrics (GE)

Key needs for a further emergence of membrane technology



By replacing thermally driven processes with membrane approaches ……

….. over an order of magnitude reduction in energy use might be achieved!

W.J. Koros, AIChE Journal, 50 (2004) 2326.

Reverse Osmosis

For desalination, seawater treatment produces over 100 millions gallons per day with 50% feedwater recovery by using 65 bar feed pressure.
An optimized thermal distillation plant with the same feed water requires 73 kwh/m^3, while a state-of-the-art RO system has an energy cost (thermal equivalent) of 6.7 kwh/m^3

….. the membrane option is over 10-fold more efficient than the thermal approach!

W.J. Koros, AIChE Journal, 50 (2004) 2326; D.H. Marks et al., National Research Council, National Academy Press, Washington, DC, 2004; T. Pankratz & J. Tonner, Lone Oak Publishing, Houston, TX, 2003.

Microfiltration & Ultrafiltration

For dilute feeds (< 15 vol. %) energy costs typically range around to 7.6 kwh/m^3 of water removed, which is roughly *10-fold savings* over competitive thermal removal by flash evaporation (~73 kwh/m^3)

W.J. Koros, AIChE Journal, 50 (2004) 2326.

Integration RO + Fuel Cells

At the current level of development, fuel cells' efficiency reach about 50-60%, against 33% for optimized heat cycles for electricity generation

….. coupling Reverse Osmosis with Fuel cells, it would overall show an improvement > 16-fold than the thermal alternative!

W.J. Koros, AIChE Journal, 50 (2004) 2326.

New High-Performance Membranes

For large osmotic pressure, higher temperature, more aggressive organic feeds: more robust membranes and modules than that currently used for water feed stream; new generation hybrid membranes and modules with improved selectivity and robustness but retaining their attractive cost advantages!

….. organic/inorganic hybrid membranes, contain the selectivity and strength of inorganics and carbons, and the processability and flexibility of polymers!

Contribution of Membrane Science to Water Desalination and Wastewater Treatment and Reuse

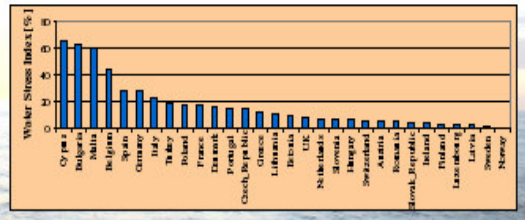
Water reuse is a growing practice in many regions of the world, even in countries that are not typically considered to have problems with water scarcity but in which the continuous growth in population, in the standard of life, in tourist infrastructure and industrial development have increased water consumption and the stress on water supplies.

In some of the countries of the Mediterranean and Middle East area, the renewable water resources per capita have seen a reduction of up to about 80% in the last 10-15 years, and the forecasts are for an increased water scarcity in many regions around the globe by the year 2020

Projected areas of water stress in the world in 2020

G. Wade Miller, Integrated concepts in water reuse: managing global water needs, Desalination, 187 (2006) 65–75

Half of the European countries, representing 70% of the population, are facing water stress issues today.

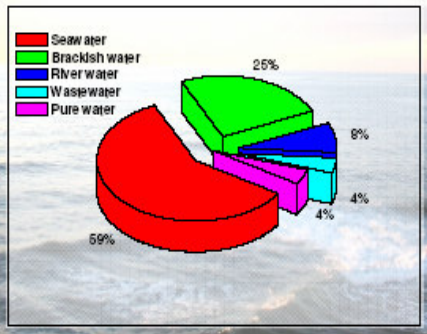


Water stress index = ratio of a country's total water withdrawal to its total renewable freshwater resources

- values less than 10%, water stress is low;
- values within the range of 10–20% indicate that investments are needed to provide adequate supplies;
- values above 20% indicate comprehensive management efforts to balance supply and demand.

D. Bixio et al., Wastewater reuse in Europe, Desalination, 187 (2006) 89–101

Global desalting capacity by sources



IDA Worldwide Desalting Plants Inventory, May 2000

Section A:

Membrane Technology for Wastewater Treatment and Reuse

Applications of Reclaimed Water

- Industrial reuse (such as use in cooling towers, for boiler feed, and for use in the cooling cycles of power plants)
- Irrigation of edible and non-edible agricultural crops
- Indirect potable reuse, such as groundwater recharge
- Irrigation of golf courses and lawns

Advantages in the use of reclaimed water

- To reduce demand of water source by recycling purified water
- To treat wastewaters to limit environmental pollution

Wastewater Treatment Technologies

- Conventional activated sludge treatment process (CAS)
- Pressure-driven membrane separation processes:
  - ✓Microfiltration (MF)
  - ✓Ultrafiltration (UF)
  - ✓Integrated Membrane Systems (IMS), combining MF or UF with Reverse Osmosis (RO) or Nanofiltration (NF)

Advantages of membrane technology compared to conventional activated sludge process

- Total retention of the biomass regardless of its properties (size of floccules, age, etc.)
- Very high quality of treated water

The trend goes for Integrated Membrane Systems (IMS) which offer:

- feasibility
- process reliability
- plant availability
- modularity
- lower operating costs

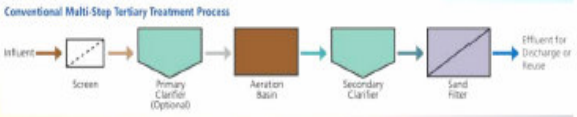
Some membrane types for Integrated Membrane Systems:

- Memcor or Zeeweed for continuous MF
- Norit/X flow, Aquasource, Zee weed-UF Pall and Koch for UF

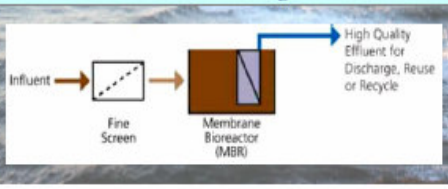
Membrane Bioreactor (MBR), a process combining membrane filtration with biological treatment…

…considered by the European Union as one of the **Best Available Technologies (BAT)*** for municipal and industrial wastewater treatment

*http://eippcb.jrc.es



MBR is operated in a similar manner as the conventional activated sludge process but without the need for secondary clarification and tertiary steps (like sand filtration). Low-pressure membrane filtration, either MF or UF, is used to separate effluent from activated sludge.



The main advantages of MBRs compared to conventional activated sludge systems are:

- **Compactness.** MBR is up to 5 times more compact than a conventional activated sludge plant because the membrane module replaces the clarification tank
- **Decreased sludge production**
- **Considerable level of physical disinfection** (the membrane is an absolute barrier for bacteria and, in the case of UF also for viruses)

MBR technology is particularly well suitable for:

- recycling of wastewater
- stringent discharge regulations
- effluents with high COD and/or ammonium loads
- sensitive receiving water bodies
- sludge which is hard to settle
- upgrading existing plants
- compact installations
- nuisance (e.g. odour) problems
- disinfection of water

Since the early MBR installations in the 1990s, the number of MBR systems has grown considerably.

Total European revenue for the MBR market was around **40 million euro in 2005 with a steady growth rate of 9%**

The majority of currently operating and commissioned plants are small- to medium size.

Commercially available systems are:

- the package treatment plant Clereflo MBR (Conder Products, UK), designed to service populations up to 5000
- the ZeeMOD® (Zenon Environmental Inc.) which is available for flow rates of up to 7500 m^3/d

The entry of membrane bioreactors into large sized projects was slow.

The use of MBRs in medium to large-scale domestic wastewater applications is growing since the last couple of years.

The main factors that contributed to MBRs development were:

- the experience gained with pilot/small-scale projects
- the cost reduction of membranes
- the improvements in their performance

Municipal wastewater treatment projects with MBR technology in Europe

Location	Size [m³/d]	Type of membranes	Start-up
Villefranque, FR*	168	Dégrémont, BRM1®	1997
Rodingen, DE	2,400	Zenon	1999
Perthes en Gatinais, FR	1,400	Zenon, BIOSEP ® process	1999
Markranstadt, DE	3,600	Zenon	2000
Swanage, UK	12,720	Kubota	2000

*Municipal projects with the reuse of reclaimed water

Location	Size [m³/d]	Type of membranes	Start-up
Campbeltown, UK	2,678	Zenon	2001
Ile de Yeu, FR	2,200	Zenon, BIOSEP ® process	2001
Thelus, FR	185	Zenon, BIOSEP ® process	2001
Collegno, IT*	960	Zenon, ZW500®	5/2001
Westbury, UK	3,536	Kubota	2002
Lowestoft, UK	14,160	Zenon	2002
Brescia, IT	42,000	Zenon, ZeeWeed® MBR	2002
Torreele, Belgium	7,000	Zenon, ZeeWeed®	6/2002
Playa Blanca, Lanzarote, SP	1,500	Zenon, ZeeWeed® 1000	

*Municipal projects with the reuse of reclaimed water

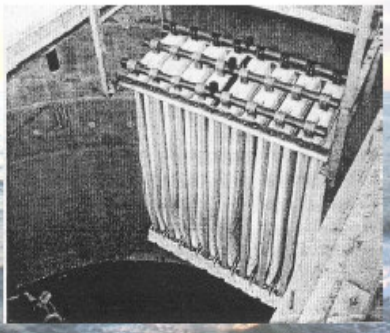
Location	Size [m³/d]	Type of membranes	Start-up
Monheim, DE	2,400	Zenon	2003
Schilde, BE	6,520	Zenon	2003
Kaarst, DE	45,144	ZeeWeed®, Zenon	2003
Rocca Imperiale, IT*	960	Zenon, ZW500®	5/2003
Waldmossingen, DE	2,160	Zenon	2004
Guilvinec FR	2,600	Kubota	2004
La Bisbal, SP	3,240	Zenon	2004
Riells I Viabrea, SP	5,160	Kubota	2004
Uerikon, CH	5,200	Zenon	2004
Cardigan, UK	8,640	Kubota	2004
Buxton, UK	10,627	Zenon	2004
Varsseveld, NL	18,120	Zenon	2004
Ballyclaire, UK	7,000	Zenon	8/2005

*Municipal projects with the reuse of reclaimed water

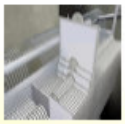
Examples of Membrane Bioreactor

Type of reactor	Type of wastewater	Application
BIOSEP (Submerged membrane bioreactor)	Municipal and industrial	Reduce BOD Removal of solids, nitrogen, phosphorous, etc.
Aerated MBR (Biofilms attached to membrane)	Industrial	COD and ammonia removal
Moving bed biofilm MBR (Submerged membrane)	Municipal	Separate biomass, colloids, soluble organic matter
Zeewed (Zenon – submerged MBR)	Domestic and pharmaceutical effluents	Reduce COD
Kubota membrane activated sludge	Urban	Reduce BOD

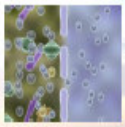
Biosep® Submerged Membrane Bioreactor



The Copa MBR Technology® is based on the *Kubota* flat sheet membrane



Kubota Flat Sheet Membranes



The membrane operates in the ultra filtration range

Tank with four membrane units

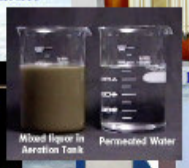
Membrane units are aerated by a coarse bubble system

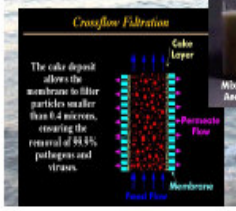
Enviroquip's Submerged Membrane Bioreactor

Removal capacity

- ✓Average pore size of membrane is 0.4 mm
- ✓Coliform bacteria larger than 0.4 mm
- ✓Build up of biofilm reduces effective pore size below 0.1 mm
- ✓Viruses are generally porcelies attached to bacteria so removed with bacteria
- ✓Removal rates for bacteria and viruses are > 99.9%

Incorporates Kubota Membranes

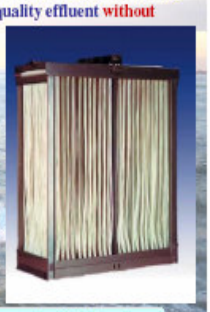




Source: http://enviroquip.com/membrane/ss1/index.htm

Case study 1: Brescia Wastewater Treatment Plant, Italy

The northern Italian city of Brescia upgraded its wastewater treatment facility by retrofitting a portion of the existing facilities with Zenon ZeeWeed® membrane bioreactor (MBR) technology that achieves a higher quality effluent without expanding the plant's footprint.



- ✓Capacity: 41,800 m3/d
- ✓Membrane Type: ZeeWeed®
- ✓Nominal pore size of membrane: 0.04µm (providing an absolute barrier to biomass, bacteria and viruses and ensuring the consistent production of high quality effluent)

Source: http://www.zenonenv.com

Wastewater and effluent characteristics

	Raw water	Quality of water requested by D.Lgs. 152/99 tab.1	Effluent from ZeeWeed® system
BOD_5 (mg/l)	255	<25	10
COD (mg/l)	505	<125	20
SST (mg/l)	292	<35	N.R. - 2
TKN (mg/l)	50		
NH_5-N (mg/l)			0,5 - 2,0
NO_5-N (mg/l)			4 - 7
P_{tot} (mg/l)	8		1 - 2

N. R.: Not rilevable

The ZeeWeed® MBR system places the membranes directly into the bioreactor tank, which drastically reduces the required plant footprint by eliminating the need for secondary clarifiers. The effluent from the plant is safely discharged into a local water supply, with the possibility of reusing the water for irrigation.

Case study 2: IWVA, Station Torreele Wastewater Treatment Plant, Belgium

The Belgian Intermunicipal Water Company of the Veurne Region (IWVA) selected a system which included ZeeWeed® membranes of ZENON, followed by reverse osmosis (RO) and ultraviolet (UV) disinfection.

The IWVA Station Torreele tertiary plant produces 7,000 m^3/d treated water, equivalent to nearly 40 percent of the annual drinking water requirements for this area.

The system constantly meets the drinking water regulatory limits for parasites and salts.

Source: http://www.zenonenv.com

Case study 3: Nordkanal/Kaarst Wastewater Treatment Plant, Westphalia, Germany

Peak Capacity: 48,000 m^3/d

Commissioned: December 2003

The existing plant employed conventional activated sludge technology, which included primary clarification, nitrification / denitrification, and sedimentation tanks.

By replacing the conventional plant with a ZeeWeed® MBR, the quality of the entire canal is restored and the environment in the City of Kaarst is improved.

Source: http://www.zenonenv.com

Case study 4: Playa Blanca Tertiary Treatment Plant, Spain

Playa Blanca uses ZeeWeed® 1000 ultrafiltration system for treating sewage treatment secondary effluent source with average turbidity of about 25 NTU with peaks of up to 50 NTU.

This is a two Process Train Plant, designed to produce a continuous nominal treated water output of 1,500 m^3/d.

Source: http://www.zenonem.com

Research and Directives at the European Union Level

The importance of municipal wastewater reuse has been acknowledged by the Commission of the European Communities through the financial support of a series of research projects in the Fourth (1994–1998), Fifth (1999–2002) and Sixth Framework Programme on Community activities in the field of research, technological development and demonstration (RTD).

EU funded projects concerning municipal water reuse

Acronym	Title
FP4 (1994-1998)	
COLD WSPS	Development of low-cost methods for treatment and reuse of drainage and urban wastewater by adaptation of waste stabilitation ponds for extreme continental climates (cold wsps)
CATCHWATER	Enhancement of integrated water management strategies with water reuse at catchment scale. Utilisation of groundwater desalination and wastewater reuse in the water supply of seasonally stressed regions
BIOWATSYST	A system approach to wastewater biotreatment for the protection of Mediterranean coastal areas

(continued)

D. Bixio et al., Wastewater reuse in Europe, Desalination, 187 (2006) 89-101

FP5 (1999-2002)	
CORETECH	Development of cost-effective reclamation technologies for domestic wastewater and the appropriate agricultural use of the treated effluent under (semi-) arid climate conditions
POSEIDON	Assessment of technologies for the removal of pharmaceuticals and personal care products in sewage and drinking water facilities to improve the indirect potable water reuse
MBR - RECYCLING	Water Recycling and Reuse by Application of Membrane Bioreactors: Textile and Municipal Wastewater as Examples
WAM-ME	Water Resources Management under Drought Conditions: Criteria and Tools for Conjunctive Use of Conventional and Marginal Waters in Mediterranean Regions
AQUAREC	Integrated concepts for reuse of upgraded wastewater
P-THREE	Removal of persistent polar pollutants through improved treatment of wastewater effluents
MEDWATER POLICY	Policy initiative to overcome water competition between the vital economic sectors of agriculture and tourism in the Mediterranean
SWIMED	Sustainable water management in Mediterranean coastal aquifers: recharge assessment and modelling issues
FP6 (2003-2006)	
AQUASTRESS	Mitigation of Water Stress through new Approaches to Integrating, Management, Technical, Economic and Institutional Instruments
MEDINA	Membrane-based Desalination: An Integrated Approach

In the sphere of the Sixth Framework Programme of the European Community, a work programme, still in negotiation phase, is

Membrane-based Desalination: An Integrated Approach

acronym MEDINA ....

... a project based on the integration of different membrane operations which will aim at improving the overall performance of membrane-based water treatment processes

List of Participants

Participant name	Country
University of Calabria	Italy
Anjou Recherche – Veolia Water	France
UNESCO – IHE	The Netherlands
KIWA	The Netherlands
Universität Duisburg-Essen-IWW	Germany
Ben Gurion University	Israel
Centre National de la Recherche Scientifique:	France
a) Laboratoire d'Océanographie Biologique b) Laboratoire de Chimie de l'Eau et de l'Environnement	
INSA Toulouse	France
Octave	France
GVS S.P.A.	Italy
University of Technology, Sidney	Australia
University of New South Wales	Australia
Carl von Ossietzky University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment	Germany
Ecole Nationale d'Ingénieurs de GABES / Institut Supérieur des Etudes Technologiques de SFAX	Tunisia

The Council of the European Union, in order to achieve a high level of protection of the environment and to prevent or to reduce emissions in the air, water and land, has adopted the IPPC Directive 96/91/EC.

This directive lays down a framework requiring Member States to issue operating permits for certain installations carrying on industrial activities. These permits must contain conditions based on best available techniques (BAT).

Source: http://eippcb.jrc.es

The European IPPC Bureau (EIPPCB) produces BAT reference documents (BREFs) that Member States are required to take into account when determining best available techniques.

A Reference Document on BAT is that in *Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector*. In this document MBR is considered as one of the *Treatment Techniques Associated with BAT for Biological Treatment Techniques.*

In many other BREFs, membrane technology is considered either as a Best Available Technology or as an Emerging Technique….

….*Emerging techniques*: those that can not (yet) be considered BAT due to the stage of development of these techniques but that are researched because they look promising for future applications, even if there is not enough information available on full scale operations. Nevertheless, in due time, *they will be qualified as BAT.*

BREFs in which membrane technology is considered as a BAT or as an Emerging Technique

Reference Document on Best Available Techniques in the Pulp and Paper Industry
Reference Document on the application of Best Available Techniques to Industrial Cooling Systems
Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry
Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry
Reference Document on Best Available Techniques for the Tanning of Hides and Skins
Bref for Mineral Oil and Gas Refineries
Bref in the Large Volume Organic Chemical Industry
Reference Document on Best Available Techniques on Emission from Storage
Reference Document on Best Available Techniques for Large Combustion Plants
Reference Document on Best Available Techniques in Food, Drink and Milk Industries
Bref for the Waste Treatments Industries

Section B:

Assessment of Membrane operations for…..

….. *water desalination*

Progress of RO Seawater Desalination Plants

	1980s	1990s	2000s
Recovery %	25	40 - 50	55 - 65
Operational pressure MPa	6.9	8.25	9.7
Product water quality TDS mg/L	500	300	< 200
Energy consumption kWh/m^3	12	5.5	4.6

I. Moch, Pre-prints of ADA Conference in Lake Tahoe (2000).

Unit product costs for the RO process depend on capacity:

0.55 $/m³ for installations with a capacity of 110,000 m³/d

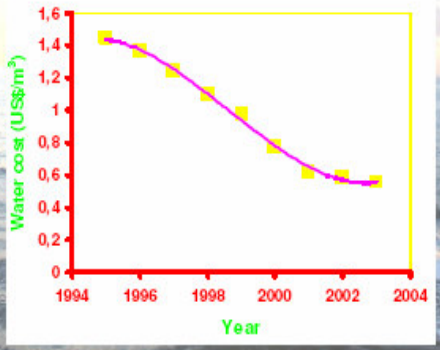
0.83 $/m³ for installations with a capacity of 40,000 m³/d

1.22 $/m³ for installation with a capacity of 20,000 m³/d

The average unit product costs for MSF, MEE and MEE-TVC are higher than for RO, with an average of 1.5 $/m³ and about 3.22 $/m³ for MVC

Data from: Elkomey *et al.*, December 2002, pp. 32-39, www.cepmagazine.org

Water cost from membrane desalination systems



Installed World desalination capacity

Process	Installed capacity (Billion Gall/day)
Reverse Osmosis (RO)	3.7
Multi Stage Flash (MSF)	3.4
Electrodialysis (ED)	0.5
Vapour Compression (VC)	0.4
Nanofiltration (NF)	0.37
Multi Effect Distillation (MED)	0.32

Israel - Jordan

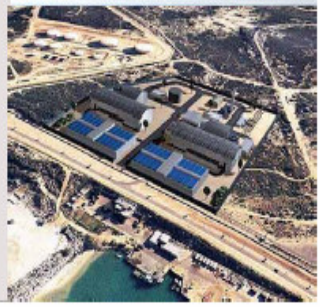
The "Red Sea – Dead Sea" Canal

850 million m³ / year

The hydrostatic energy potential of 300 m elevation difference will be used for desalination by hydrostatically supported SWRO

Ashkelon desalination plant

When completed will be the largest of its kind in the world



Key-factors for further improvement of RO desalination systems

- Enhancement of the water recovery factor
- Costs reduction
- Improvement of the water quality
- New brine disposal strategy

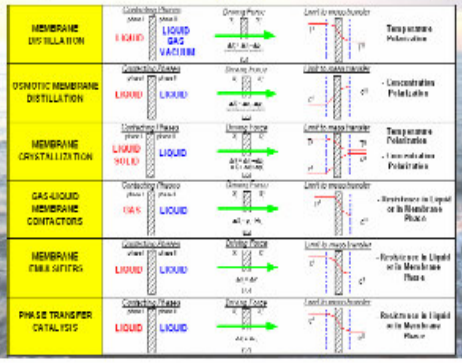
Section C:

Contribution of Membrane Science to produce high-tech devices and processes .....

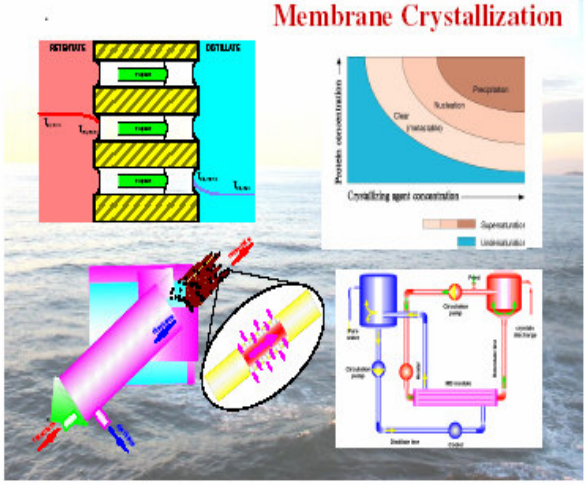
.....membrane contactors technology

Membrane contactors

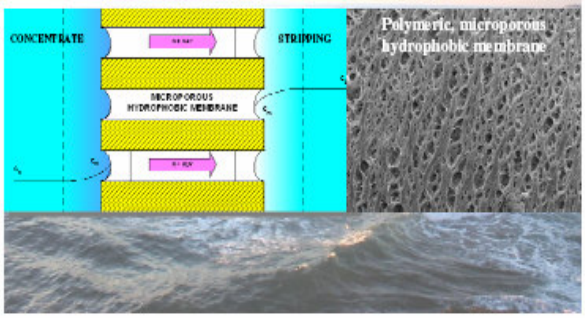
Among separation techniques involving membranes, membrane contactors (MC) are expected to play a decisive role for the design of alternative production systems appropriate for sustainable growth.



Membrane Crystallization



Membrane crystallization (MCr) has been recently proposed as one of the most interesting and promising extension of the membrane distillation process



Driving force: *vapor pressure difference*

$$p(c,T)=p^0(T)a(c,T)$$

temperature difference → *thermal membrane crystallization*

concentration difference → *osmotic membrane crystallization*

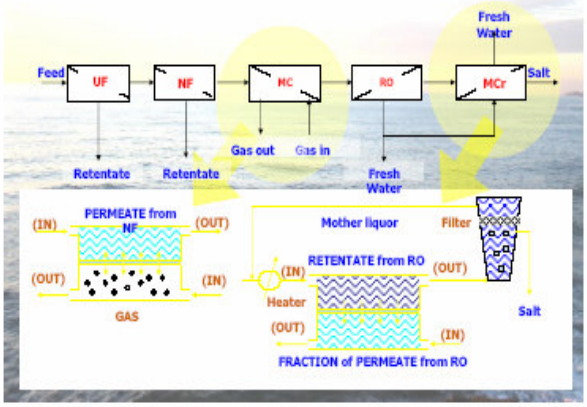
→ supersaturated solution

→ nucleation and crystal growth

Advantages of Membrane Crystallization compared to traditional techniques

- ✓ High specific area for mass transfer
- ✓ Optimal control of the supersaturation level
- ✓ Shorten induction periods
- ✓ High values of the crystal growth rate at low supersaturation
- ✓ Possibility to act on the heterogeneous nucleation choosing appropriate polymeric membrane
- ✓ Well ordered organization of the molecules, finally resulting in the formation of crystals with better structural properties, when working under forced solution flow regime

Integrated membrane system with membrane contactors in seawater desalination



Membrane Crystallization in water desalination

Disadvantages of RO:

- Seasonal variations is seawater quality might cause difficulties in process control
- Needs for frequent chemical cleaning to prevent efficiency loss in the process
- Sensitivity of membranes to fouling
- Damage of membranes by oxidizing compounds
- Scaling by e.g. $CaCO_3$, $CaSO_4$, $BaSO_4$

Feed pre-treatment is an imperative demand

Trouble-causing agents

Damaging

- Acids, bases
- pH-value
- Bacteria
- Free oxygen

Blocking

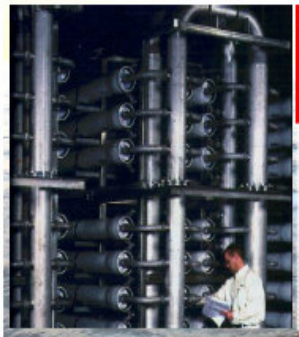
Fouling

- colloids
- metal oxides (Fe^{2+}, Mn^{4+})
- bacteria, microorganisms

Scaling

- $CaCO_3$
- $CaSO_4$
- $BaSO_4$
- $SrSO_4$
- CaF_2
- $MgCO_3$
- SiO_2

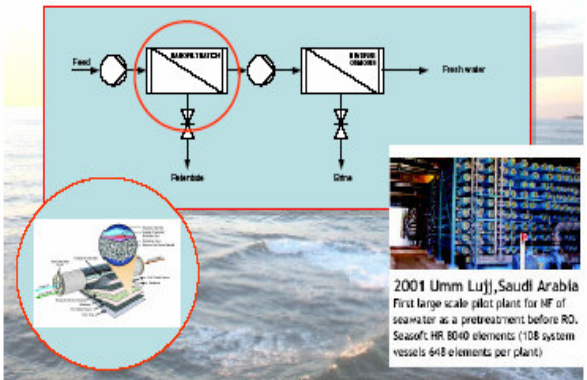
MF/UF Pre-treatment



In 1995 it was estimated that less than 25 MGD installed capacity was in operation in North America; five years later that number has grown to over 400 MGD.

About seven different MF/UF manufacturers are based in the USA, Japan, France, the Netherlands and Canada. MF and UF systems in the 2 to 4 MGD capacity range are priced at about $0.45 per gallon of capacity; MF/UF systems capable of 25 to 40 MGD are priced at about $0.25 per gallon of capacity.

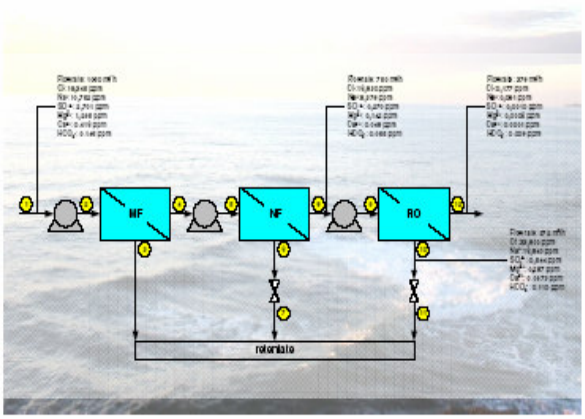
Coupling NF and RO systems



2001 Umm Lujj,Saudi Arabia
First large scale pilot plant for NF of seawater as a pretreatment before RO. Seasoft HR 8040 elements (108 system vessels 648 elements per plant)

Water recovery factor increases up to 50%!

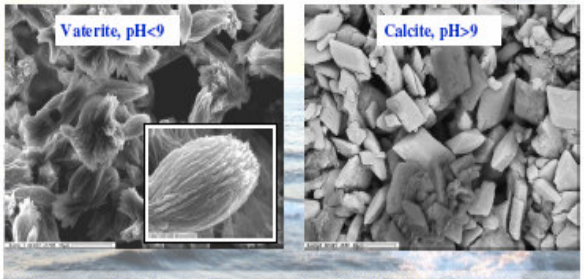
Case 1 – MF-NF-RO (FS1)



Case 2 – MF-NF (MCr)-RO - (FS 2)

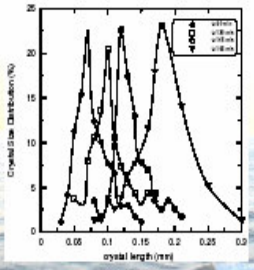
The introduction of a membrane-crystallization unit downstream the NF retentate (FS2) increases the global water recovery factor of water up to 58.6%, although increases the unit cost up to \$0.80/m^3 as consequence of additional expenses for membrane replacement, chemicals and steam. However, this gap is potentially offset by 8.4 M\$/yr resulting form the production of 8,7 tons NaCl/h (0.044\$/kg) and 2.1 tons Epsomite/h (0.33\$/kg)

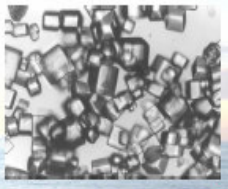
Spontaneous precipitation of calcium carbonates from artificial NF retentate water resulted in the formation of vaterite at pH< 9, while calcite is the phase precipitating at higher pH



Calcium carbonate can be removed up to 89% (at pH = 9.90 and up to 95% by additional cake filtering at pH = 9.00), recovering up to 2.95 kg $CaCO_3$/m^3 NF from the precipitator; the total reduction of Ca^{2+} ions varied from 56% to 89%

NaCl Crystallization by Membrane Crystallizer





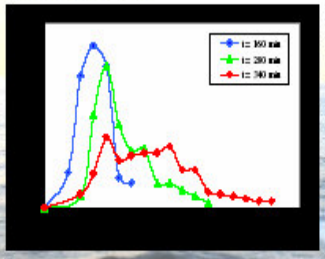
$$CV = \frac{STANDARD\ DEVIATION}{MASS\ BASED\ MEAN\ SIZE} = \sqrt{\frac{\mu_2 \cdot \mu_0}{\mu_1^2} - 1}$$

COEFFICIENT OF VARIATION: 15 - 30%
Typical CV in conventional mixed-suspension crystallizer: ~ 50%

35.5 kg of NaCl per cubic meter of NF retentate, representing the 78% of the total amount of dissolved sodium chloride, are produced if the solution is concentrated to 32.5 times with respect to initial composition

Epsomite Crystallization by Membrane Crystallizer

Epsomite crystallized in orthorhombic form, showing an acicular structure stretched along c-axis.



GROWTH RATE: $1.2 \cdot 10^{-8}$ m/s (DC=0.17 $g_{Epsomite}/100gH_2O$)

8.4 kg $MgSO_4 \cdot 7H_2O$ per cubic meter of NF reject can be produced by the integrated membrane system

Case 3 – MF-NF-RO (MCr) - (FS 3)

When the membrane crystallizer works on RO retentate (FS3) the global water recovery factor of water increases up to 70.1%, and both cost and environmental impact of brine disposal operations are drastically reduced. The additional production of 12,5 tons NaCl/h might counterbalance the higher unit cost of water production (4.3 M\$/yr, \$0.72/m^3)

Case 4 – MF-NF (MCr)-RO (MD) - (FS 4)

If a membrane crystallizer works on the NF retentate and a membrane distillation unit on the RO brine (FS4) the global water recovery factor of water increases up to 88.%, and both cost and environmental impact of brine disposal operations are drastically reduced. The additional production NaCl, CaCO3 and $MgSO_4 \cdot 7H_2O$ might counterbalance the higher unit cost of water production

Case 5 – MF-NF (MCr)-RO (MCr) - (FS 5)

In FS5, two membrane crystallizers works both on NF and RO retentate: the global water recovery factor of water increases up to 92.8%, and both cost and environmental impact of brine disposal operations are drastically reduced. The additional production NaCl, CaCO3 and $MgSO_4 \cdot 7H_2O$ might counterbalance the higher unit cost of water production

Comparison of the various integrated membrane system configurations proposed

	FS1	FS2	FS3	FS4	FS5
Electrical energy (kWh/h)	1,913	1,913	1,913	1,913	1,913
$E_{x,in}$ (kJ/h)	9,005,787	10,438,035	10,339,868	11,765,246	11,772,116
$E_{x,out}$ (kJ/h)	2,787,244	2,032,326	1,633,518	2,244,652	1,030,028
ε (%)	30.95	19.47	15.80	19.08	8.75

Exergy (*Ex*) is defined as the maximum useful work that a system can do when it passes reversibly from an actual state to the reference state, where it is in equilibrium with the surroundings

Exergetic efficiency

$$\varepsilon(\%) = \frac{Ex_{output}}{Ex_{input}} \cdot 100$$

Comparison of the various integrated membrane system configurations

	FS1	FS2	FS3	FS4	FS5	MSF
Unit cost water production ($/m³)	0.46 0.39[b]	0.68-0.55[a] 0.63[b]-0.51[a,b]	0.59-0.47[a] 0.54[b]-0.43[a,b]	0.74-0.59[a] 0.71[b]-0.51[a,b]	0.73-0.54[a] 0.69[b]-0.51[a,b]	1.27-1.1
$CaCO_3$ produced[b] (kg/m³)	-	1.19	0.12	0.96	1.00	-
NaCl produced[b] (kg/m³)	-	9.79	16.86	7.91	20.35	-
$MgSO_4 \cdot 7H_2O$ produced[b] (kg/m³)	-	1.25	0.00	1.01	0.96	-

	FS2	FS3	FS4	FS5
$CaCO_3$ ($/yr)	437,000	41,730	478,700	437,000
NaCl ($/yr)	1,743,000	2,949,000	4,693,000	1,743,000
$MgSO_4 \cdot 7H_2O$ ($/yr)	4,218,000	-	4,218,000	4,218,000
Total annual cost per m³ of water produced ($/m³)	-0.40 / -0.52[a]	0.077/-0.041[a]	-0.49 / -0.68[a]	-0.13 / -0.32[a]
Total annual cost per m³ of water produced[b] ($/m³)	-0.44 / -0.57[a]	0.032/-0.086[a]	-0.53 / -0.71[a]	-0.16 / -0.36[a]

(a) if thermal energy is available in the installation or the stream is already at the operating temperature of the MCr unit.

(b) if a Pelton turbine is used as energy recovery device.

Conclusion

- Membrane technology has led to significant innovation in processes and products over the last few decades offering new opportunities in the design, rationalization and optimization of innovative productions.
- At present, the most interesting developments for membrane technologies in water desalination industry are probably related to the possibility of integrating various membrane operations, with overall important benefits in the logic of process intensification strategy.
- Reclamation and reuse of seawater and wastewater represent an important water supply in many areas of the world, particularly in Europe, US and Australia, able to solve the increasing municipal, industrial, and agricultural demands for water.

Conclusion

- The use of reclaimed water has the advantage to reduce wastewater treatment and disposal costs, to decrease the discharge of pollutants to the environment and to provide water of a high-quality.
- Numerous pilot plant studies and commercial facilities operating all over the world have demonstrated the technical and economic feasibility of reclaiming municipal wastewater treatment plants effluents through pressure-driven membrane separation processes.
- In this yield, MBR technology has the potentiality to become the key element for wastewater reuse, because it has several advantages compared with conventional activated sludge plants such as reliability, compactness and optimal treated water quality.

TREATMENT OF CAMPUS WASTEWATERS BY MEMBRANE BIOREACTOR FOR POTENTIAL REUSE IN IRRIGATION

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Abstract

Pilot-scale experiments were conducted in treating wastewaters from university campus area using a membrane bioreactor (MBR) (ZW-10, Zenon Environmental Inc.) unit containing an immersed hollow fiber membrane module. The unit was continuously operated aerobically to achieve nitrification and carbon removal. During the six months of operation, samples were taken from raw wastewater and permeate for chemical oxygen demand (COD), biological oxygen demand (BOD_5), total organic carbon (TOC), NO_3-N, NO_2-N, NH_3-N, total kjeldahl nitrogen (TKN), total nitrogen (TN), total phosphorus, total suspended solids (TSS), turbidity, total dissolved solids, conductivity, pH, fecal coliform, total coliform, and total organism analysis. Feed and permeate flowrates, permeate flux, transmembrane pressure (TMP), air flowrates, and dissolved oxygen, temperature, pH, conductivity, MLSS levels in the bioreactor were frequently measured. A routine backpulse regime (15 s after each 10 min of permeate production) was employed by reversing the permeate pump and using the collected permeate. Although the influent characteristics were highly variable and the wastewater temperatures were as low as 6 ^oC during winter months, MBR system continuously performed very well throughout its operation. The treatment performance and permeate quality were not negatively affected by such variations. Permeate quality obtained during the 6-month period is as following: COD: <10 mg/L, BOD_5: <2 mg/L, TSS: <1 mg/L, NH_3-N: <0.9 mg/L, NO_3-N: <35 mg/L (no denitrification employed), TKN: <3 mg/L, turbidity: <0.1 NTU, fecal coliform: <15 cfu/100 mL, total coliform: <120 cfu/100 mL, total organism: <280 cfu/100 mL. The high quality permeate was obtained independent of variable operational conditions including sludge retention time, hydraulic retention time, permeate flux (ranging between 23 and 39 L/m^2-h), wastewater temperature, and organic loadings. No chemical cleaning was performed during the six months of operation, except routine backpulses with permeate. However, continuous aeration was employed (1-2 ft^3/min) to scour membranes and provide enough dissolved oxygen (2-4 mg/L) for bio-oxidation. The high quality permeate water will be tested for agricultural irrigation in campus area in the next phases of the project.

This work was supported by a Research Grant (İÇTAG-Ç086 103I033) from the Scientific and Technical Research Council of Turkey (TUBITAK).

Treatment of Campus Wastewaters by Membrane Bioreactor for Potential Reuse in Irrigation

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Nevzat Ö. Yiğit, Grad. Res. Assistant
İlker Harman, Grad. Res. Assistant
Gökhan Civelekoğlu, Grad. Res. Assistant

Süleyman Demirel University, Dept. of Environmental Engr., Isparta, Turkey

NATO/CCMS Pilot Study on Clean Products and Processes, Annual Meeting,
Special Topical Symposium on Water Reuse and Recycling
May 10, 2006 Istanbul

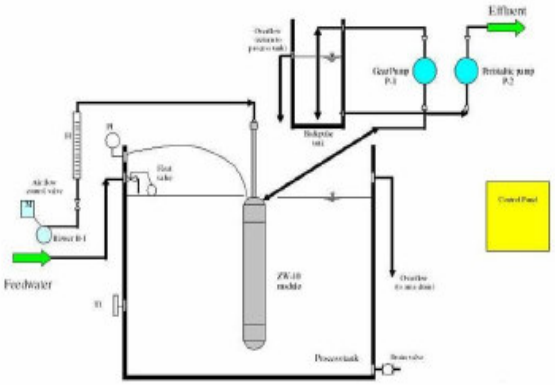
Motivation/Objectives

- To investigate the treatability of domestic wastewater from university campus area with diurnally and seasonally variable characteristics using a pilot-scale membrane bioreactor (MBR).
- About 30K students in the campus
- Wastewater flow: 1000-5000 m^3/day
- Variable wastewater characteristics
  - Infiltration- wet weather
  - Student population variations: holidays, etc
  - Cleanings in dormitories, restaurants, etc=>dilution
- Potential future reuse in the campus: irrigation

MBR Unit

- Immersed MBR system: ZW-10, Zenon Environmental Inc.
- 230-L HDPE single process tank
- ZeeWeed 10® hollow fiber MF module: 0.9 m^2 active membrane area
- Reversible permeate pump for suction and backpulse
- Capacity: 380-1500 L/day
- 1000-L feed tank & 1000-L permeate collection tank
- Blower: 119 L/min.
- Continuously operated aerobically for 8 months (Jan-Aug. 2005)

MBR Unit



Organic carbon removal + nitrification

Approach

- Three major operational phases:
  1) no sludge wastage, normal flux: 23-25 L/m^2-h
  2) SRT: 20 d, normal flux: 23-25 L/m^2-h
  3) SRT: 20 d, high flux: 36-39 L/m^2-h
- A routine back-pulse regime (15 s after each 10 min of permeate production)
- Continuous aeration (2-4 mg/L DO)
  - Membrane scour
  - Bio-oxidation
- Impacts of HRT, SRT, operating flux on treatment performance, permeability and fouling

Parameters

- Raw wastewater and permeate:
  - flowrate, COD, BOD_5, TOC, NO_3, NO_2, NH_3, TKN, TN, TP, TSS, TDS, conductivity, turbidity, pH, fecal coliform, total coliform, and total organism
- MBR:
  - TMP, DO, air flowrate, MLSS, MLVSS, Temp, pH, conductivity
  - membrane permeability, net, instantaneous and temperature corrected flux, F/M ratio, organic loading rate, and specific substrate utilization rate

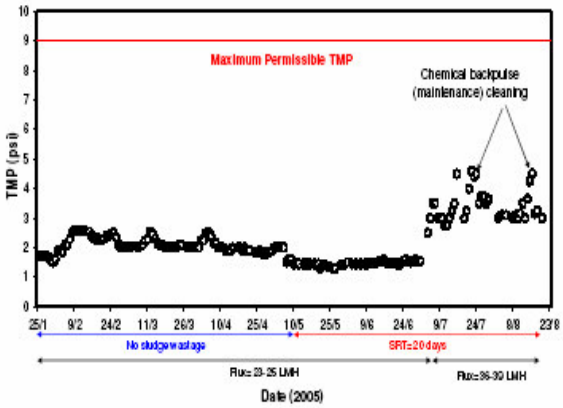
Influent Characteristics

Parameter	Influent Average (Min.-Max.)	Permeate Average (Min.-Max.)
BOD_5 (mg/L)	205 (95-380)	1.5 (1-6)
COD (mg/L)	316 (105-695)	9.5 (5-60)
NH_3-N (mg/L)	24 (7-44)	1.0 (0.1-10.5)
NO_3-N (mg/L)	14.5 (5.5-37.5)	32.0 (16.0-45.5)
NO_2-N (mg/L)	0.7 (0.1-1.6)	0.5 (0.1-2.6)
TKN (mg/L)	34 (18-52)	1.7 (0.1-3.6)
TN (mg/L)	49 (29-70)	34 (18-48)
TSS (mg/L)	109 (52-276)	0.6 (0.3-1.3)

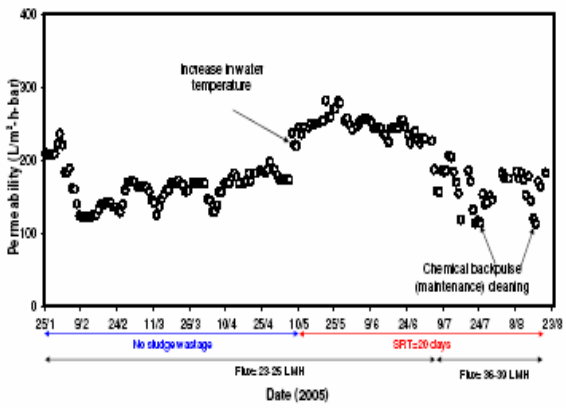
Influent Characteristics

Parameter	Feed Average (Min.-Max.)	Permeate Average (Min.-Max.)
Turbidity (NTU)	90 (40-213)	0.08 (0.02-0.41)
Conductivity (µs/cm)	1441 (642-8300)	1329 (556-4190)
pH	7.91 (6.95-8.32)	7.74 (7.36-8.26)
MBR Temperature (°C)	18.8 (6.6-25.5)	
Total organism (cfu/100 mL)	1.67×10^{10} (8.0×10^{8}-6.0×10^{10})	2.5×10^{2} (6.0×10^{1}-1.06×10^{3})
Total coliform (cfu/100 mL)	5.4×10^{9} (6.0×10^{7}-2.0×10^{10})	1.6×10^{2} (4.0×10^{1}-8.4×10^{2})
Fecal coliform (cfu/100 mL)	5.8×10^{8} (1.0×10^{7}-3.0×10^{9})	1.9×10^{1} (2.0×10^{0}-1.4×10^{2})

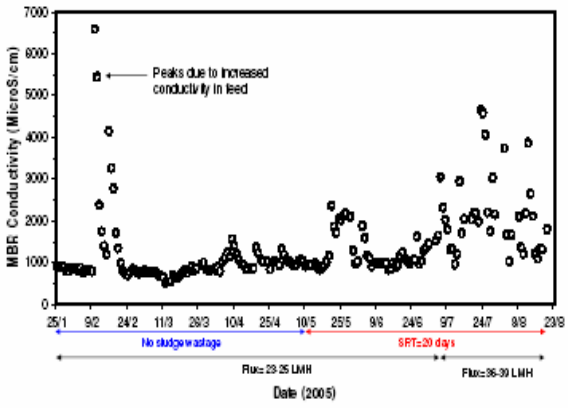
Operational Conditions vs TMP
(irreversible fouling not observed)



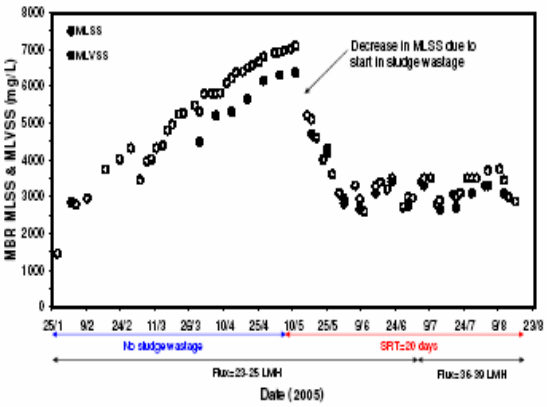
Operational Conditions vs K



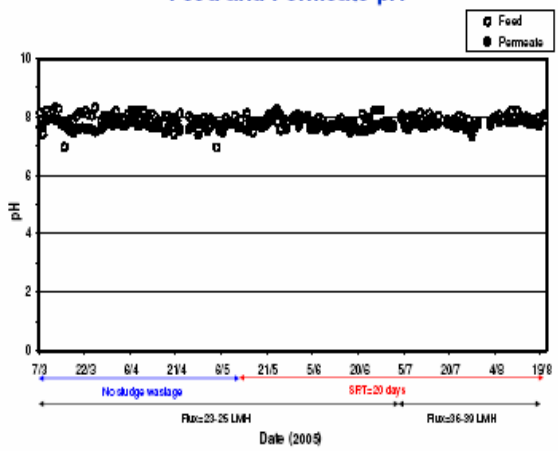
Conductivity in MBR



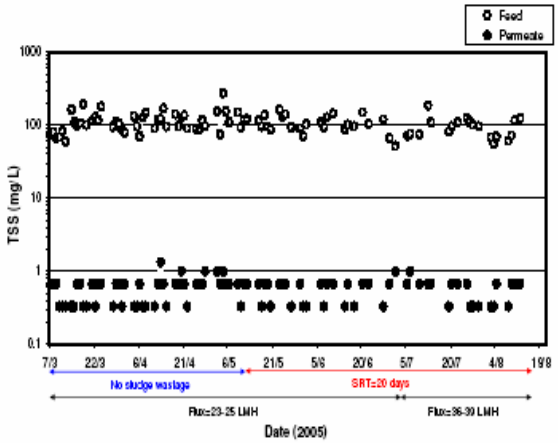
MLSS in MBR



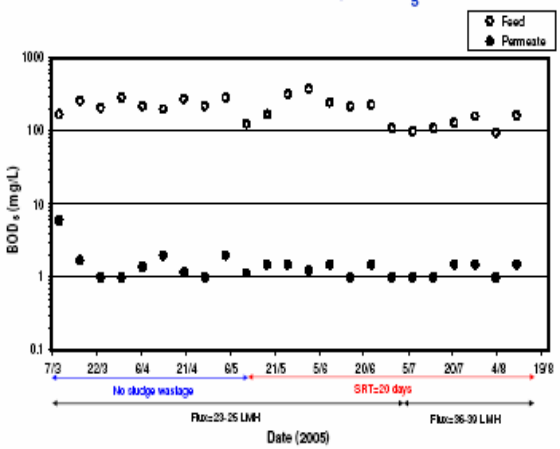
Feed and Permeate pH

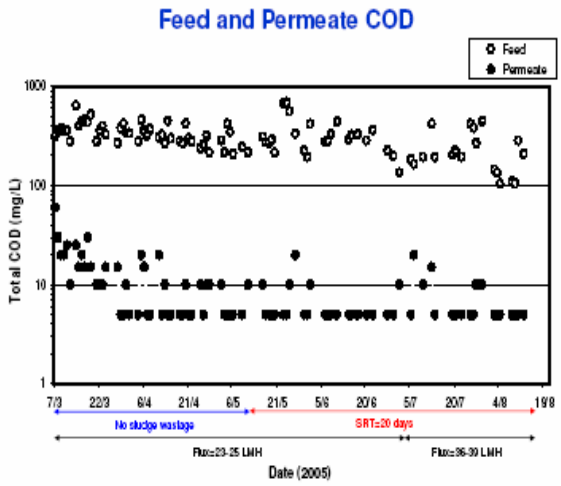


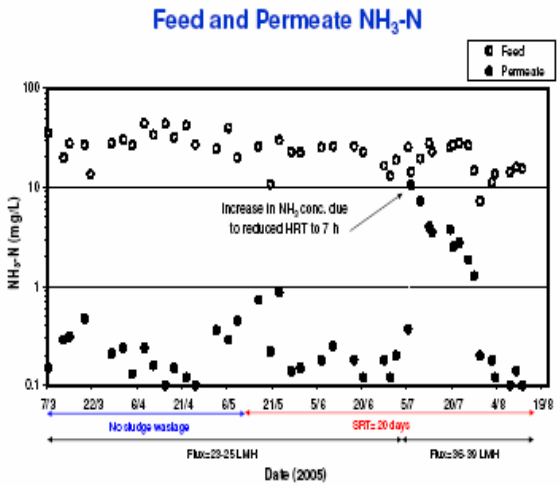
Feed and Permeate TSS

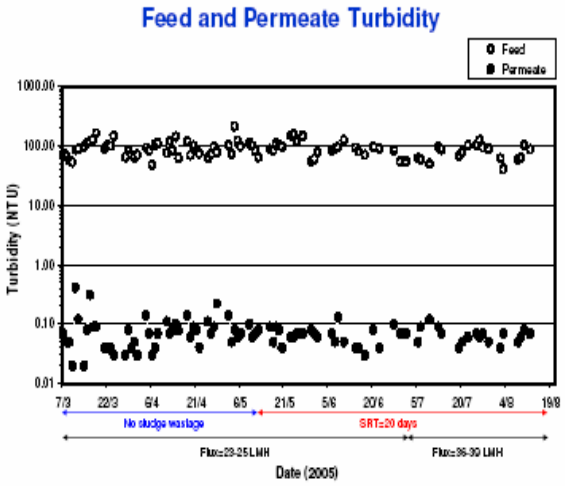


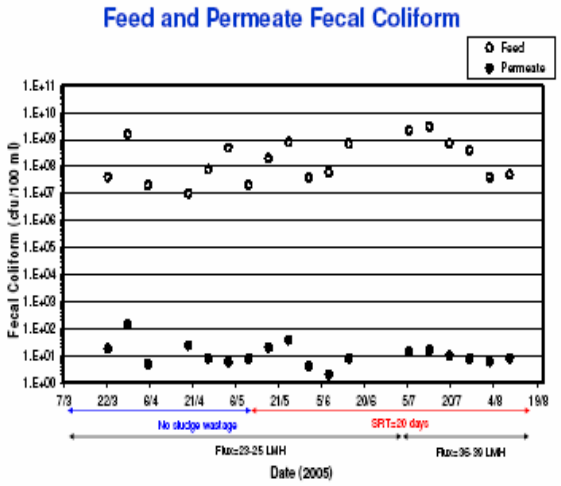
Feed and Permeate BOD_5

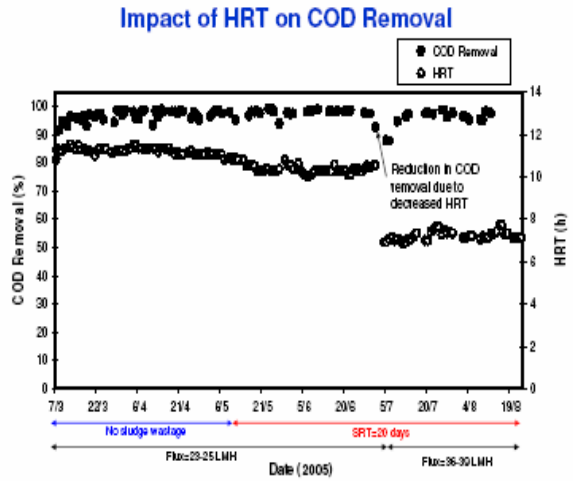


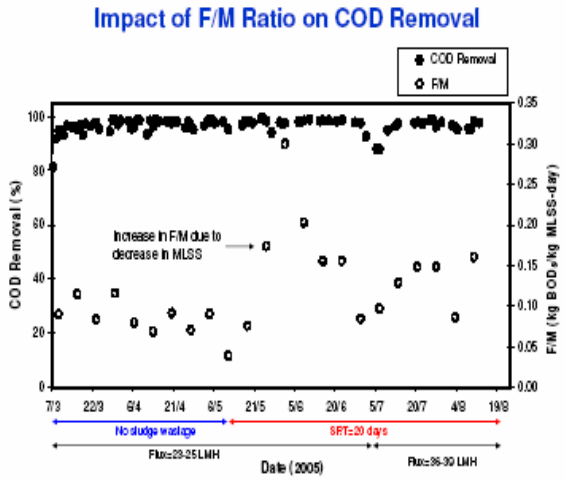

Feed and Permeate COD
Feed
Permeate
Total COD (mg/L)
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)


Feed and Permeate NH3-N
Feed
Permeate
NH3-N (mg/L)
Increase in NH3 conc. due to reduced HRT to 7 h
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)


Feed and Permeate Turbidity
Feed
Permeate
Turbidity (NTU)
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)


Feed and Permeate Fecal Coliform
Feed
Permeate
Fecal Coliform (cfu/100 ml)
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)


Impact of HRT on COD Removal
COD Removal
HRT
COD Removal (%)
HRT (h)
Reduction in COD removal due to decreased HRT
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)


Impact of F/M Ratio on COD Removal
COD Removal
F/M
COD Removal (%)
F/M (kg BOD5/kg MLSS-day)
Increase in F/M due to decrease in MLSS
No sludge wastage
SRT=20 days
Flux=23-25 LMH
Flux=36-39 LMH
Date (2005)

Conclusions

- Variable influent characteristics,
- Temps as low as 6 ºC, peaks in TDS:
  - Very good treatment performance,
  - Sustainable carbon removal & nitrification independent of F/M, organic loading rate, HRT, SRT, MLSS, and permeate flux tested,
  - Tolerated variations=> wide spectrum of specialized biomass.
- Irreversible fouling not observed. No consistent reduction in permeability.
- No chemical cleaning required @ flux of 23-25 LMH for 6 months.

Conclusions

- Consistent >6 logs bacteria removal + <0.1 NTU turbidity => membrane integrity √
- Will guide the decision on a potential full-scale MBR application and reuse of the treated wastewater for irrigation in campus area.

- **This work was supported by a Research Grant (İÇTAG-Ç086 103I033) from the Scientific and Technical Research Council of Turkey (TUBITAK).**

TEXTILE WASTEWATERS: WATER REUSE AND DYSTUFF REMOVAL AND/OR DERGRADATION

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Abstract

Large quantities of water are used for textile dying operations. Currently most of the water is discharged because there are not available suitable options for water recovery and reuse. These wastewaters contain significant amounts of unreacted dyestuff and other chemicals (i.e. sodium chloride). Due to the current practice of mixing the wastewaters from different dying operations is very difficult to recover the dyestuff and reuse the wastewaters. Reactive dystuffs are more difficult to be removed as the conventional wastewater treatment plants, which rely on sorption and aerobic biodegradation, have low removal efficiency for them.

In the current research project the possibility of removing the unreacted and or hydrolysed dystuff and reusing the wastewater after each dying operation has been studied. Dispersed-air column flotation was used as the separation process. Flotation is a relatively simple process capable of removing flocs almost totally, as well as lowering turbidity. It exploits the natural or induced hydrophobicity of the dyestuff when a stream of gas bubbles is introduced into a dispersion or solution. The hydrophobic material adheres to bubble surfaces and floats to the top of the liquid phase, forming a froth layer rich in solute. Surface-active chemicals (surfactants), termed collectors, are often used to artificially induce hydrophobicity, in some cases selectively, so as to remove from solution only the desired or undesired substances.

The influence of pH, background electrolyte and surfactant concentration was studied. Alkaline pH, high collector concentration and high sodium chloride concentration had a positive effect on dyestuff removal. Cetyl-trimethyl-ammonium bromide was found to be effective as collector. A first order model adequately described the flotation kinetics. The process was efficient and removed single dyestuffs (Remazol Brillantrot 3BS, Gelb 3RS 133% and Blue RN new) as well as mixture of them. From initial concentrations of 100 mg/L the remaining single dyestuff concentration was less than 1 mg/L (which is the discharge limit). From mixtures of the above (100 mg/L each) the remaining dyestuff concentration was less than 300 ADMI units (the discharge limit for mixtures). The wastewater treated by flotation was successfully reused in dying operations. The concentrated dyestuff from the flotation column was degraded successfully with advanced oxidation with power ultrasounds (20 kHz frequency). The experiments were considered successfully and a full scale experiment was proposed.

Textile wastewaters:
water reuse and dystuff removal and/or degradation

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Division of Chemical Technology

NATO/CCMS, 7-12 May 2006, Turkey

ORIGIN OF COLOUR

(I. Dye manufacturing industry)

- ~10^5 dyes
- ~$7X10^5$ t/y
- ~2% discharge

(II. Dye consuming industry)

- ~10% loss

PROBLEM INDICATION

- High COD
- High salt content and alkalinity
- Possible toxic effect
- Aesthetic problems
- Reduced photosynthetic activity in aquatic life due to reduced light penetration
- High volume discharge 100-500 L H_2O/Kg product

DYE-HOUSES EFFLUENTS limits

EC Directive 91/271/EEC

- COD 125 mg/L
- BOD 25 mg/L

- ~1 ppm of dye is visible

DECOLOURISATION METHODS

•Chemical (oxidative processes, ozonation, Fenton reagent, photochemical, NaOCl, Cucurbituril, electrochemical)

•Physical (sorption, membrane filtration, irradiation, coagulation, activated carbon, peat, wood chips, fly and ash coal, silica gel)

•Biological (funghi, living/dead biomass, anaerobic bioremediation)

Method	Advantage	Disadvantage
Oxidation	Rapid	High energy
Sorption	Good removal	Regeneration
Membrane	~all dyes	Sludge
Coagulation	Economical	High sludge

REACTIVE DYES

- 20-30% total market dyes
- fixation ~70%
- Low removal by sorption and aerobic degradation

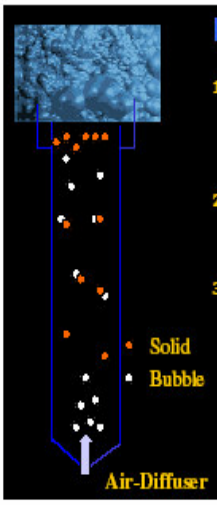
OBJECTIVE I

Removal of three reactive dyes from aqueous solutions by dispersed-air flotation

Advantages

- Simplicity
- Easy separation of phases
- Low cost
- Efficiency in treatment of high volumes
- Small RTD

FLOTATION



1. Addition of surface active reagents (collectors) to make particles/molecules hydrophobic
2. Generation of air bubbles in the bottom of the column, using air diffuser
3. Adhesion of the air bubbles to the hydrophobic particle/molecule which removed to the top of the dispersion, forming a froth rich in particles

Dyes Tested

1. Remazol Brillantrol 3BS (Red) (CI:239) λ_{max}=541 nm
2. Remazol gelb 3RS 133% (Yellow) (CI:176) λ_{max}=419 nm
3. Remazol Br blue RN new (Blue) (CI:19) λ_{max}=588 nm

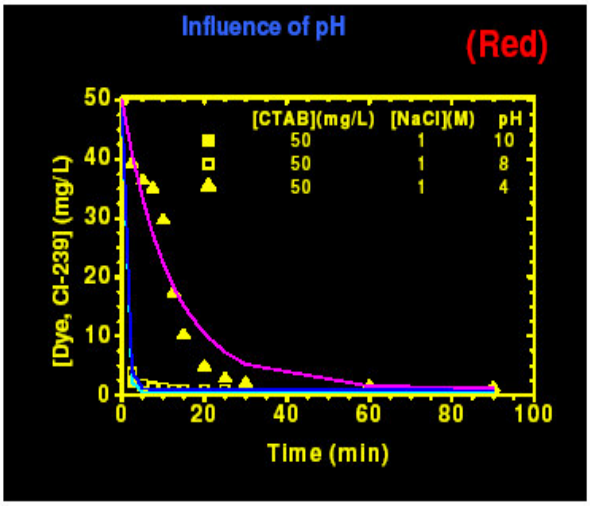
Collector (Cationic)

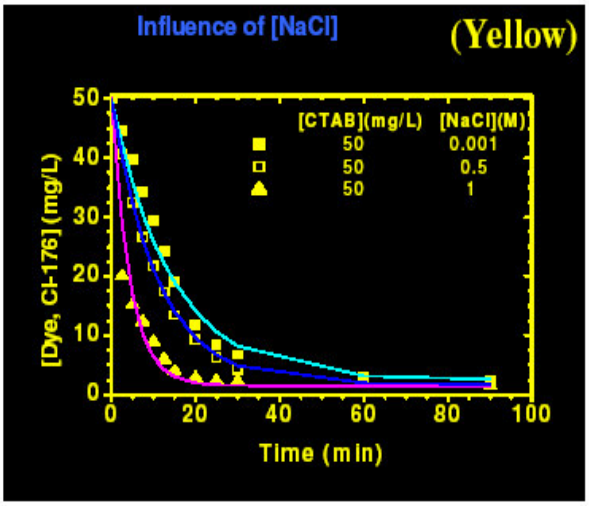
1. Cetyl Trimethylammonium Bromide (CTAB)

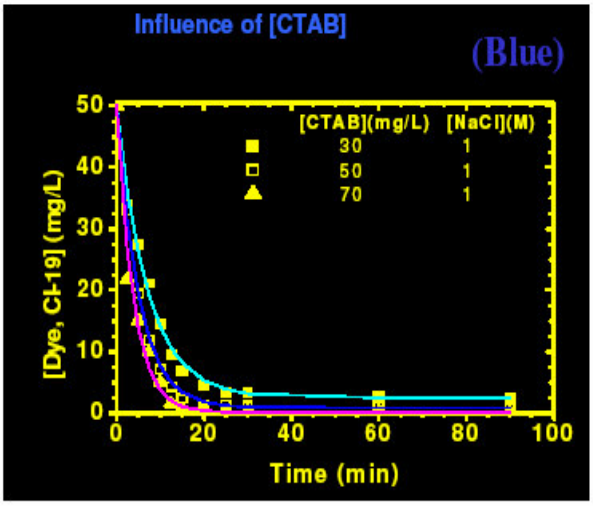
EXPERIMENTAL PROCEDURE

- [dye] (mg/L)
- [NaCl] (g/L)
- [CTAB]
- pH

- $dye^- + CTA^+ \rightarrow dye^- CTA^+$





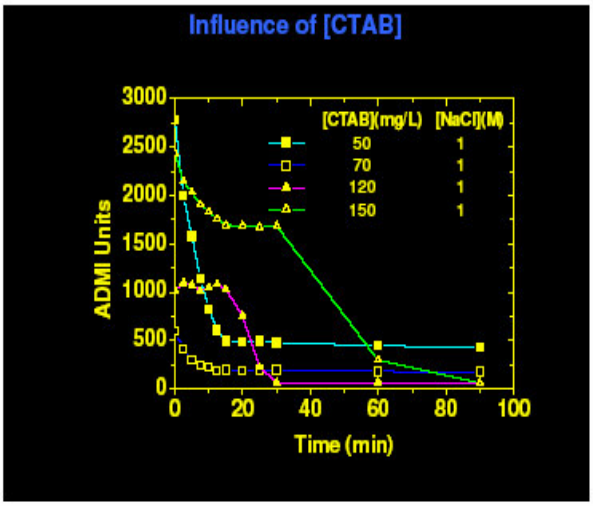


Mixture of Reactive dyes

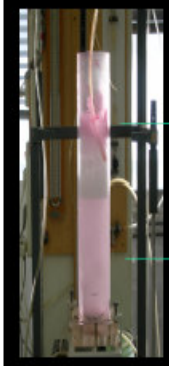
(20 ppm Red+20 ppm Yellow+20ppm Blue)

[Colour] ——→ ADMI units

US Pollutant Discharge System permit level 300 ADMI units



OBJECTIVE II



Foamate (dyestuff) Destruction

Unfixed dye has lost its bonding ability ???

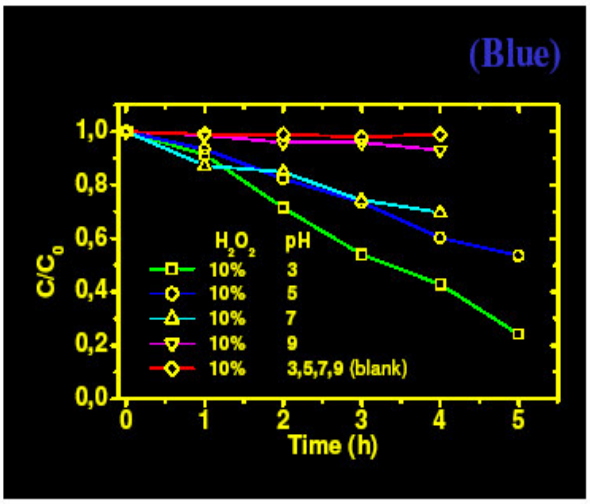
Water re-use Textile Dyeing

Water Re-use Textile Dyeing

[Dye]in	[CTAB]in
50	50
5	30
5	10
Ref	0

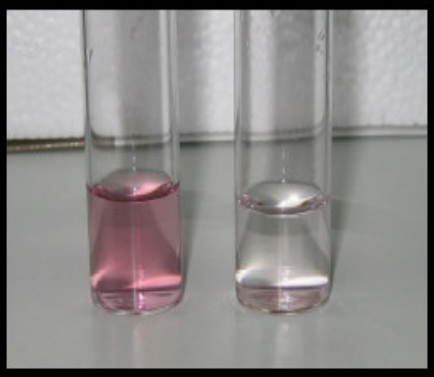
Foamate Destruction

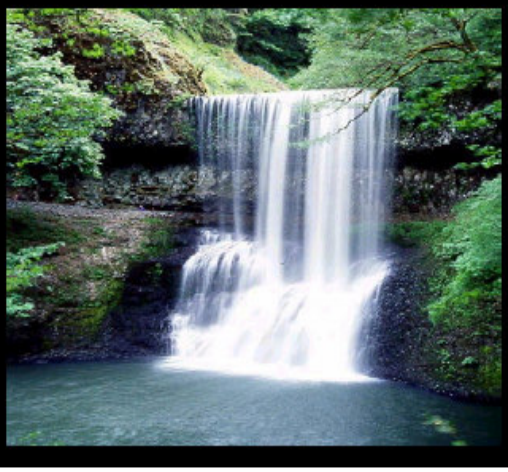
ULTRASONIC IRRADIATION



Electrochemical cell

Before and After treatment (30 mins)





Initial results

- Quick kinetics (in comparison to US)
- good color destruction (not always below the limits

combination of US and electochemical method

CONCLUSIONS

- Flotation: quick and efficient
- Cleaned water can be recycled
- Dyes destruction by ultrasounds and electrochemical cell seems promising

ACKNOWLEDGEMENTS

Thanks are due to:

Greek Ministry of Education (Pythagoras I) for the financial support

DyStar, for providing the dyes

Thank you
for your attention

WATER SEGREGATION AND REUSE IN TEXTILE INDUSTRY

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Abstract

Processes in textile industry require extensive water use. Although the industry contributes to the economical conditions of the countries it has numerous of environmental adverse effects, including discharge of high strength colored effluents to receiving waters. These impacts may be minimized by the application of the CP methodology along with the advanced wastewater treatment techniques for reuse. Moreover, implementation of a well designed pollution abatement strategy along with the reuse/recycle concept may be beneficial for economical point of view as discharge of pollutants and wastes represents extra expenditures to the enterprise. Textile sector contributes 8.4% of gross national products, has a contribution of 35-40% for the export income and constitute 10% of work power in Turkey. Turkey is considered to occupy 5th and 6th place in the world for woollen and cotton products, respectively. Water consumption in wool finishing processes is in the order of 110–650 L kg^{-1} product (UNEP, 1994). The overall textile and finishing products in Turkey is approximately 1,000,000 t year^{-1} which corresponds to about 100 million m^3/year of wastewater discharge.

Textile industry water management strategy involves reuse of water, minimization of water consumption, substitution of chemicals with environmentally sound products, recycling and recovery of chemicals, dye baths, etc. Along these lines, in this study comprehensive characterization of the applied processes and the wastes, assessment and selection of reuse/recycle CP options, wastewater treatability studies, feasibility studies and cost assessment were carried out for the selected integrated enterprise of wool-PES blends and apparel industry. The method of approach for the implementation of the CP options is presented.

Key words: Textile industry, CP application, wastewater treatment, reuse/recycle, segregation

References

1. UNEP, 1994. The Textile Industry and the Environment. UN Sales No.: E93-III-D5, ISBN 92-807-1367-1, Paris

WATER USE, REUSE, AND RECYCLING IN MICRO- AND NANO-MANUFACTURING

Farhang Shadman

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Abstract

Micro and nano-manufacturing industries demand large quantities of water at purity levels, which are unprecedented in industrial applications. The key solution to reducing water usage and wastewater discharge in the ultra-pure water (UPW) plants is the development of suitable technology for water reuse and recycling. In particular, successful water conservation strategies will require innovations in a number of areas.

The potential rapid growth of nanotechnology industry presents special environmental obstacles and technology issues. These challenges are beginning to have significant impact on both the development of new processes and the application of new materials for nano devices and nano-manufacturing.

At present, no attention has been paid to the environmental questions raised by the introduction of nano-scale particles in manufacturing, or the fate of these particles in treatment or waste effluents. One example is the case of nanoparticles in chemical mechanical polishing which could be a key driver and testbed application of the nano scale manufacturing environmental methodologies proposed in this overall program. The impact of surface planarization and cleaning on water use and reuse in high technology manufacturing is particularly significant.

In this presentation, innovations in the following areas will be discussed and reviewed:

1) *Development of low-energy and low-chemical water purification processes:* This is particularly important because many of the existing purification methods were not originally developed and optimized for applications similar to that of the semiconductor fabrication facilities.

2) *The use of innovative metrology methods for rapid detection of surges and upsets:* In this area the concept of comprehensive and integrated metrology combined with process control is key in both performance improvement and in cost reduction.

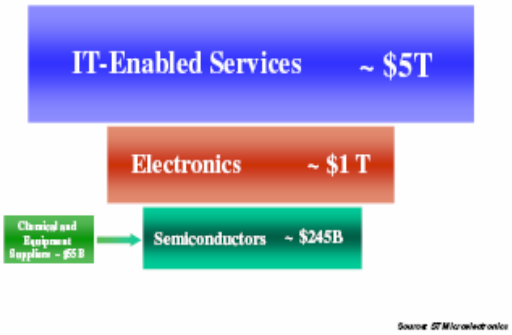
3) *Tools and techniques for risk-free recycling:* In this respect, there is need for a robust system to prevent potential risks associated with water recycling and to demonstrate that recycling, when properly designed and implemented, can save water, reduce cost, and improve water quality.

Water Use, Reuse, and Recycling in Micro- and Nano-Manufacturing

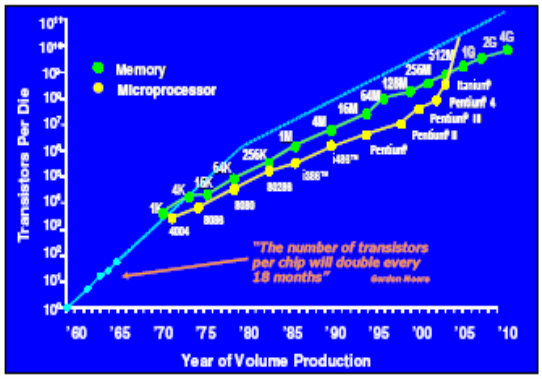
Farhang Shadman
University of Arizona

NATO/CCMS Meeting
Istanbul, Turkey
May 2006

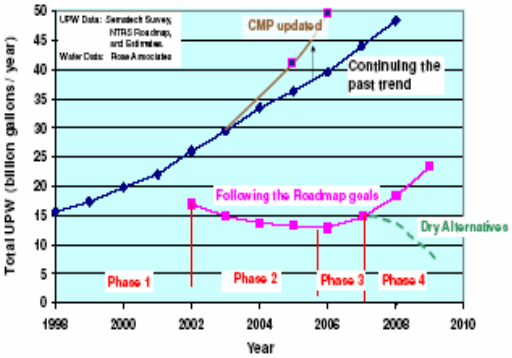
Worldwide Economic Impact of Semiconductor Industry



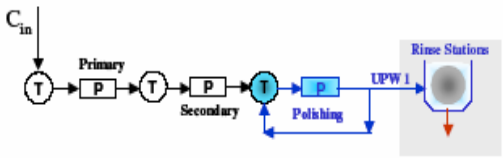
Unprecedented Technology Revolution



Water Usage in the US Fabs



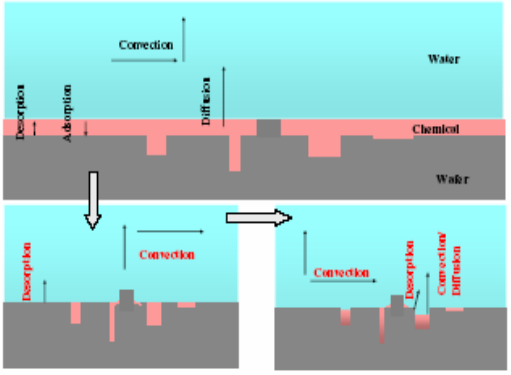
Ultra-Pure Waster Configuration in Semiconductor Plants



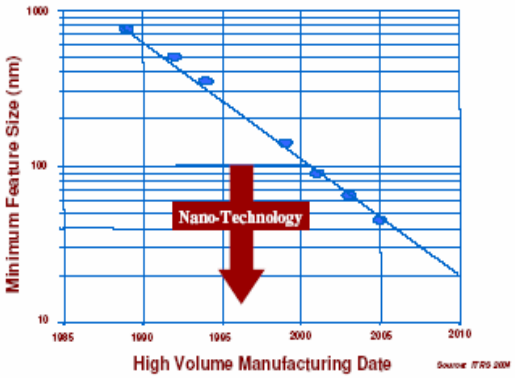
Innovations in Chemical Science/Engineering to Achieve a Sustainable Semiconductor Industry

Primary Use of Water: Cleaning and Rinsing of Micro and Nano Structures

Rinsing of Patterned Wafers

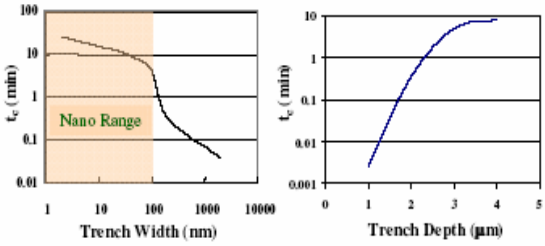


Trends in Feature Size



Impact of Nano Scaling on Cleaning

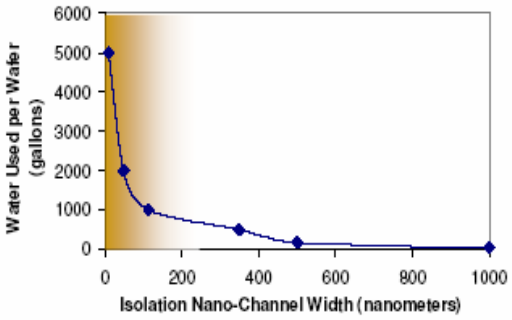
Farhang Shadman (UA)



t_c is the time needed for 99.99% clean up

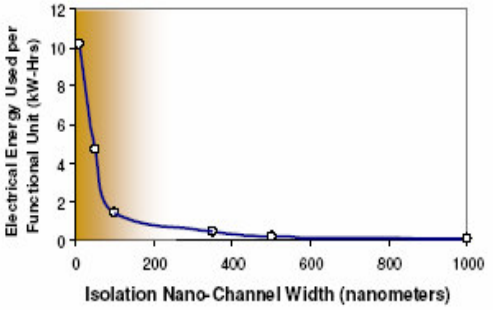
Impact of Nano-Scaling on Water Usage

Farhang Shadman (UA)

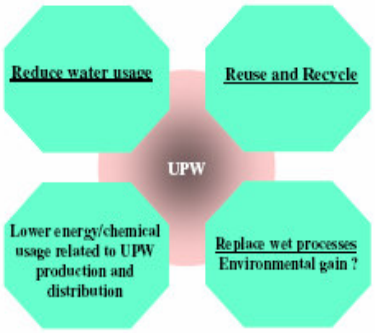


Impact of Nano-Scaling on Energy Usage

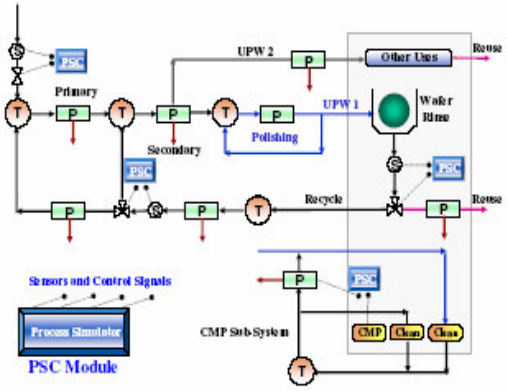
Farhang Shadman (UA)



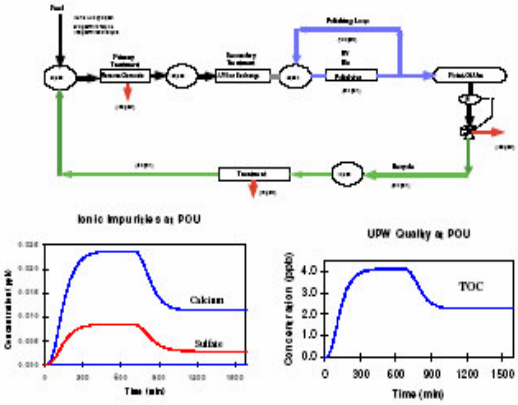
Water Conservation Strategies



Water Recycling Technology



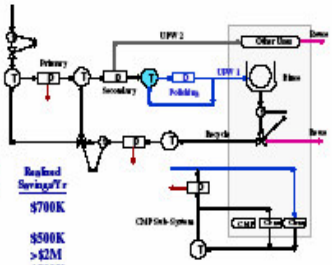
Effect of Recycle on POU Purity



New Technology for Water Recycling and Conservation

Reported Impacts of New ERC Technology (Sematech, 2001)

	Rinse Time Reduction	Water Use Reduction	Reduced Savings/Yr
Fab A, US	40 %	38 %	$700K
Fab B, US	40 %	34 %	
Fab C, US	34 %	34 %	$500K
Fab D, US	25 %	30 %	>$2M
Fab E, US	44 %	50 %	$500K
Fab F, US	25 %	25 %	$250K
Fab G, US	55 %	50 %	
Fab H, US	60 %	70 %	
Fab I, Europe	25 %	25 %	$400K
Fab J, Asia	50 %	42 %	



Water recycle technology

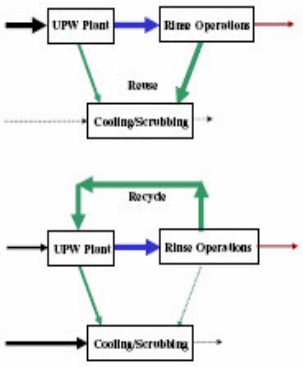
Optimization of Use/Reuse Strategies

Determining Factors:

- Purity at the POU
- Purification cost
- System & installation cost
- Real risk
- Perceived risk

Guidelines:

- Match the flow rates for supply and demand (water balance)
- Match the water quality for supply and demand (optimization)

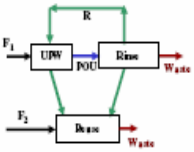


Comparison of Water Conservation Options

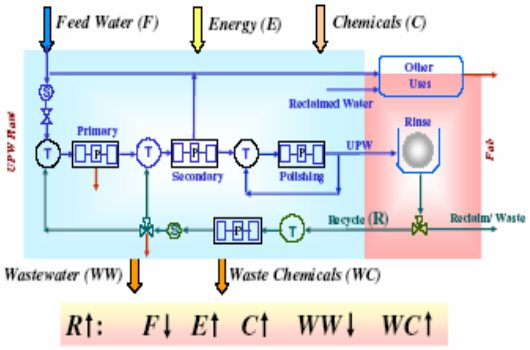
Options	Rinse (gpm)	Recycle Ratio	Waste (gpm)	Waste Conc. (TOC, ppb)	Feed, F_1 (gpm)	Feed, F_2 (gpm)	Total Feed (gpm)	POU Conc. (TOC, ppb)
Base Case*	1000	0	1000	150	1000	100	1100	11
Option 1	400	0	400	210	400	780	1180	10
Option 2	1000	50%	500	165	500	490	990	11
Option 3	500	90%	50	310	50	800	850	18
Option 4	800	70%	240	150	240	570	810	8

* Base Case: no recycle; 70% reuse.

Feed: 500 ppb TOC



UPW Production, Distribution, Use, and Reuse



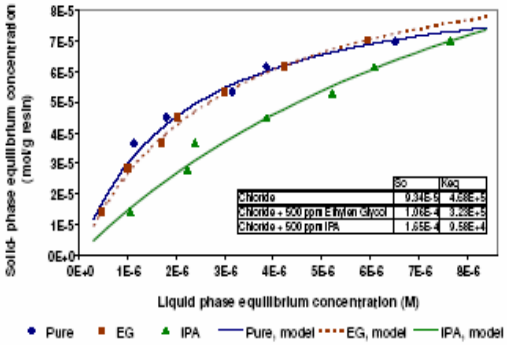
Innovations in Chemical Science/Engineering to Achieve a Sustainable Semiconductor Industry

For Feasible and Economical Recycling

We Need

Low-Energy, Low- Chemical, and Robust Ultra-Purification Methods

Effect of Organic Impurities on Ion-Exchange Performance



	So	Kaq
Chloride	9.34E-5	4.68E+5
Chloride + 500 ppm Ethylen Glycol	1.08E-4	3.28E+5
Chloride + 500 ppm IPA	1.65E-4	9.58E+4

Two Primary Processes for Removal of Organics

Oxidation

Advantages:
- Removal and not segregation

Disadvantages:
- Slow
- Energy/chemicals demand

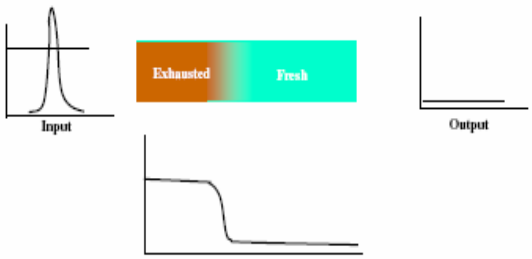
Capture (Filtration or Adsorption)

Advantages:
- Fast
- Many options

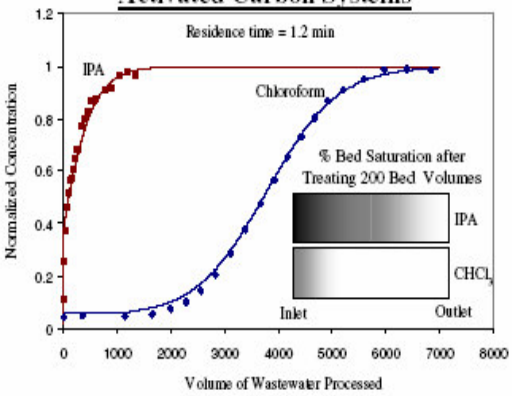
Disadvantages:
- Impurities remain in the system

The Ideal Adsorption Device

(Carbon Bed or Ion Exchange)



Compound Dependence of Purification in Activated Carbon Systems



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Multi-Component Interaction Competitive Adsorption

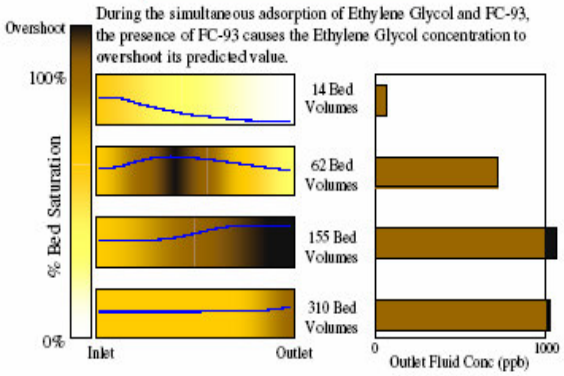

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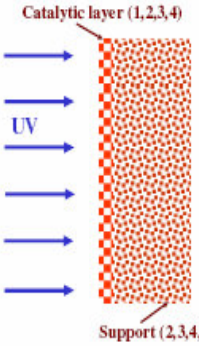
Photo-Catalytic Membrane



Functions:

1. Electron-hole pair formation
   $TiO_2 \xrightarrow{h\nu} h^+ + e^-$
2. Radical generation
   $H_2O + O_2 + h^+ + e^- = Ox$
3. Impurity adsorption
4. Oxidation reaction
   $TOC_1 + Ox \longrightarrow TOC_2 + CO_2 + H_2O$
5. Radical quenching

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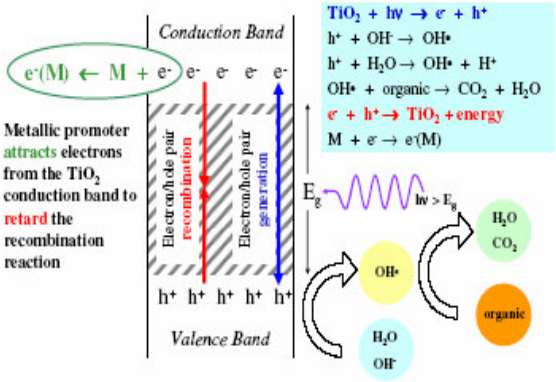
Role of Promoters in TiO_2 Catalytic Oxidation



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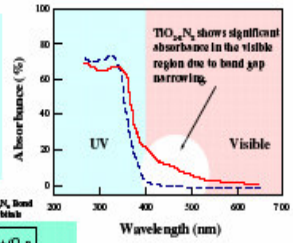
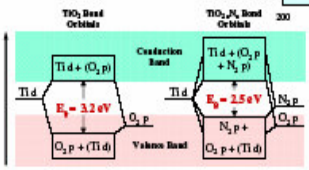
Search for Improved Promoters in TiO_2 Catalytic Oxidation

Addition of nitrogen decreases the energy band gap, thus increasing the electron-hole generation and UV utilization efficiency.





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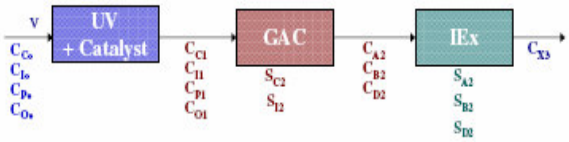
Low-Energy Hybrid Purification of Water

Shadman (UA)



$H_2O + h\nu \xrightarrow{k_1} O$
$C + h\nu \xrightarrow{k_2} I$
$C + O \xrightarrow{k_3} I$
$I + O \xrightarrow{k_4} P$

$C + X_{GAC} \underset{k_{a2}}{\overset{k_{d2}}{\rightleftharpoons}} C.X_{GAC}$
$I + X_{GAC} \underset{k_{a1}}{\overset{k_{d1}}{\rightleftharpoons}} I.X_{GAC}$
$C.X_{GAC} + O \xrightarrow{k_5} P$
$I.X_{GAC} + O \xrightarrow{k_6} P$
$C + O \xrightarrow{k_7} I$
$I + O \xrightarrow{k_8} P$
$O + GAC \xrightarrow{k_9}$ Products

$A + B.X \underset{k_{10}}{\overset{k_{10}}{\rightleftharpoons}} A.X + B$
$A.X + D \underset{k_{11}}{\overset{k_{11}}{\rightleftharpoons}} A.X.D$
$B.X + D \underset{k_{12}}{\overset{k_{12}}{\rightleftharpoons}} B.X.D$
$D + Y \xrightarrow{k_{13}} D^{*}Y$

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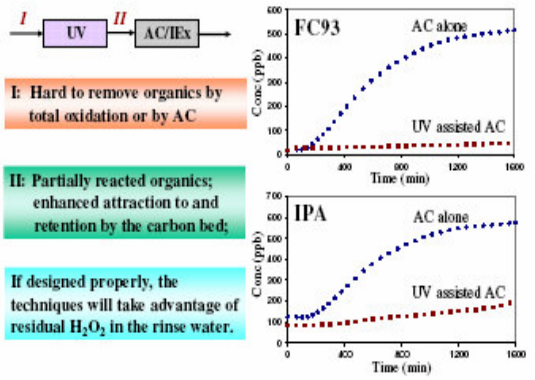
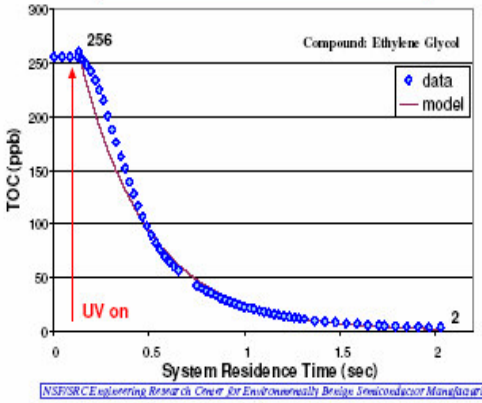
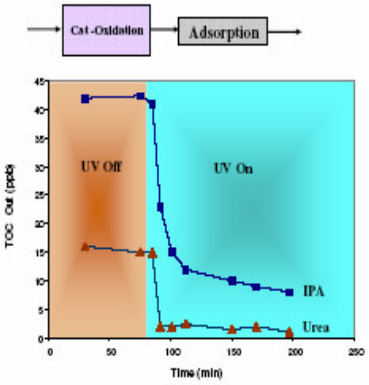
UV-Assisted TOC Removal by Activated Carbon



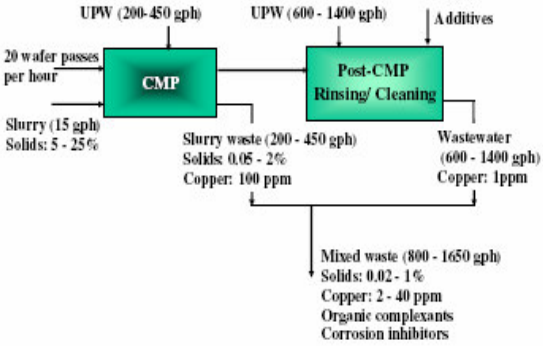
Hybrid Purification of Water



Hybrid Purification Process

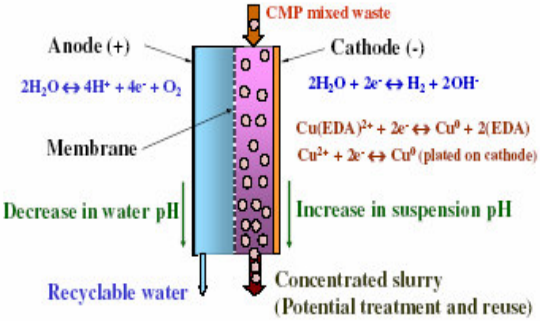


ESH Aspects of CMP and Post-CMP Cleaning



Wastewater Treatment by Electrodecantation

Raghavan, Baygents (U of Arizona)



STUDIES ON SOME SELECTED UWWTP EFFLUENTS OF TURKEY TO SEARCH THEIR REUSE POTENTIAL IN AGRICULTURE

Ayşegül Tanık

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Abstract

The effluent quality of the urban wastewater treatment plants (UWWTP) in Turkey has to obey the discharge standards stated in the National Water Pollution Control Regulation (WPCR). According to studies conducted within the framework of MEDAWARE Project, a number of 22 of these plants have been investigated in detail in terms of their satisfactory operation performance, proximity to agricultural land, and sufficient reuse potential. Most recently, another 4 plants are selected to conduct detailed analysis on the performance of the treatment plants with almost more than 30 parameters for the needs of upgrading these treatment plants as to comply with national reuse criteria for irrigation purposes. Sampling and analyses along with site visits were realized by TUBITAK-MRC (The Scientific and Technical Research Council of Turkey - Marmara Research Centre) under the coordination of ITU. In Turkey, the total number of UWWTPs under operation is 129.

The effluents of the selected UWWTPs are in general not suitable for agricultural irrigation for the time being, as at least one common water quality parameter, fecal coliform criteria in irrigation is not satisfied in almost all the selected plants. The UWWTPs have to obey the current receiving water standards that do not use any of the microbiological parameters. Therefore, some of the plants do not even have disinfection units as their final polishing treatment unit. Although some own disinfection units, but these are not satisfactorily operated due to their high energy requirement and chemical use. Besides, boron is another significant parameter used in irrigation water criteria. Like for the above mentioned treatment plants, most of the existing UWWTPs in Turkey do not face a boron problem. Sulfate concentrations together with the BOD_5 values completely lie below the stated limits of Class I water; however, chloride values demonstrate various classes of use. Conductivity values represent Class III properties in all the selected plants. Even though the national irrigation water criteria has been active since 1991 (WPCR,1991), reuse of treated wastewater for irrigation has not been considered consciously till now as the country has not yet experienced severe water shortages. In the nearest future, reuse of treated water will be one of the important environmental issues of the country.

Sustainability of irrigation in contemporary agricultural practices is being adversely affected by some constraints in Turkey that are mainly restrictions on soil, water and energy resources, changes in economic conditions & infrastructure, lack of environmental consciousness and insufficient irrigation management. In Turkey, treated domestic wastewater is used for irrigation either directly or indirectly. In arid areas in which irrigation activities should be increased for crop production, direct irrigation of untreated wastewater is commonly practiced.

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MEDAWARE

This work is a part of the project titled

"DEVELOPMENT OF TOOLS AND GUIDELINES FOR THE PROMOTION OF THE SUSTAINABLE URBAN WASTEWATER TREATMENT AND REUSE IN THE AGRICULTURAL PRODUCTION IN THE MEDITERRANEAN COUNTRIES (MEDAWARE)"

which is financially supported by the European Commission, Euro-Mediterranean Partnership, Euro-Mediterranean Regional Programme for Local Water Management.

The main objectives of the MEDAWARE project are

- To identify the prevailing situation of water resources, urban wastewater treatment and management in Turkey,
- To develop tools and database for the promotion of sustainable urban wastewater treatment,
- To improve the already existing national policy,
- To establish guidelines to be utilized by the responsible authorities on the most efficient solutions regarding the operation of the wastewater treatment systems.

Water Requirements of Turkey (Year 2000)

Year	Total (10^6 m^3)	Sectoral Requirement		
		Domestic (10^6 m^3)	Irrigation (10^6 m^3)	Industrial (10^6 m^3)
1990	43.300	5.900	32.300	5.100
1995	50.600	7.400	37.000	6.200
2000	58.100	9.000	41.800	7.300

Water Consumption in Turkey (Year 2000)

Year	Total Consumption (10^6 m^3)	Development (%)	Sectoral Consumption		
			Domestic (10^6 m^3)	Irrigation (10^6 m^3)	Industrial (10^6 m^3)
1990	30.600	28	5.141	22.016	3.443
1992	31.600	29	5.195	22.939	3.466
1995	33.500	30	5.300	24.700	3.500
2000	42.000	38	6.400	31.500	4.100
2002	38.900	36	5.700	29.200	4.000

The overall situation of water supply (Year 2000 figures)

- Turkey is divided into 3227 municipalities
- 2359 have a drinking water network
- 143 of these municipalities have a drinking water treatment facility
- Lack of infrastructure, insufficient number of treatment facilities, water leakage (32% of total supply)
- illegal water consumption (37% of total supply) hinder the efficient use of municipal water facilities (The State Planning Organization, 2001)

Assessment of rural and urban water withdrawal

Urban and Rural Water Withdrawal (State Institute of Statistics, 2001)

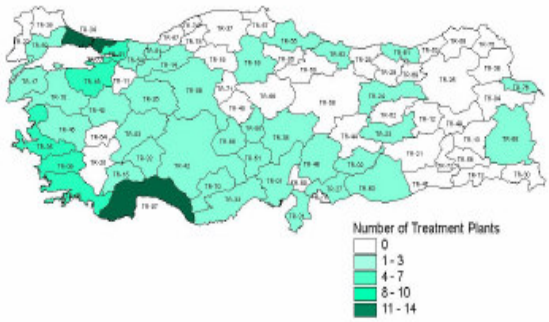
	Rural Withdrawal distribution (%) (Total water amount: 1564 x 10^6 m^3)	Urban Withdrawal distribution (%) (Total water amount: 6202 x 10^6 m^3)
Springwater	24.3	22.1
Lake	0.53	10.3
River	1.54	2.21
Dam	4.90	39.6
Groundwater	67.4	24.1
Pond	0.37	1.57
Other	0.96	0.12

The database for the realization of the project's scope was established following a step-by-step survey given as;

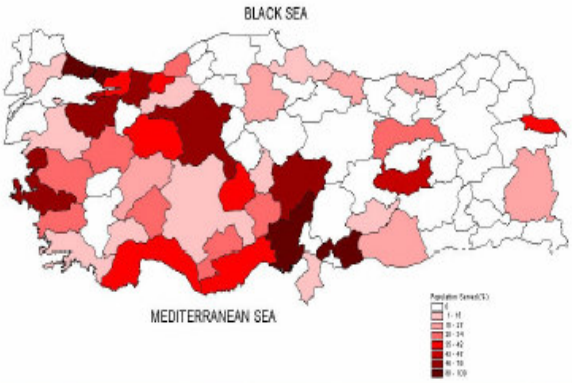
1. Identification of the population served by UWWTPs
2. Presentation of the current technologies (physical, biological and advanced) applied in the country's UWWTPs
3. Qualitative and quantitative assessment of current situation of Turkish UWWTPs
4. Prevailing effluent disposal criteria, methods and best practices
5. Reuse potential of effluent received from UWWTPs in Turkey
6. Elucidation of needs for upgrading UWWTPs to comply with the current discharge criteria

Present Situation of Turkish UWWTPs

- There are currently 129 UWWTPs in Turkey
- They serve a grand total of 30.374.000 capita
- 43 provinces have urban wastewater treatment plants
- 28 plants are located in the 12 Greater Metropolitan cities (population>100 000)
- Istanbul : 13 UWWTPs
  Antalya : 14 UWWTPs
  Kocaeli : 6 UWWTPs



Provinces of Turkey and distribution of the country's UWWTPs



Population served by UWWTPs in the provinces of Turkey

Receiving Water Discharge Standards for Domestic Wastewater

There are 5 tables in the revised regulation based on population.

Class 1: Population 84-1 000
Class 2: Population 1 000-10 000
Class 3: Population 10 000-100 000
Class 4: Population > 100 000

Example: Class 4

Parameter	Unit	Composite Sampling (2 hours)	Composite Sampling (24 hours)
BOD_5	mg/L	40	35
COD	mg/L	120	90
TSS	mg/L	40	25
pH	-	6-9	6-9

• The parameters in all Classes are same, but the values become stricter as the population increases.

Effluent Discharge Methods and Practices in Turkey

Effluent Disposal Method	Number of Plants	% of Total Number of Plants	Total Effluent Flow (m^3year^{-1})	% of Total Effluent Flow
Land (Agricultural Area)	17	13	131,319,517	13.2
Dams, Lakes	10	8	68,622,832	7.8
Coastal and Marine	49	38	1,150,746,062	38.0
Streams, Rivers and Creeks	53	41	732,780,646	41.1
Total Numbers	129	100	2,083,469,057	100.0

Reuse Potential of UWWTP Effluent in Turkey

- Although the Turkish legislation on wastewater reuse in agriculture has been established in 1991, there is no major improvement in the realization since then.
- Only few applications exist in small communities where domestic wastewater is used for irrigation of forest areas, gardens and parks.
- There are several planning procedures for the treatment of urban wastewater and its reuse for agricultural irrigation.
- Treated effluent originating from Ankara UWWTP is used for irrigation of several crops.
- Konya province known as the "grain cellar" and the largest agricultural area of the country. Currently there are planning efforts of using Konya UWWTP effluent for the irrigation of cereals.
- A comprehensive, regional project known as the Southern Anatolia Project (In Turkish: Guneydogu Anadolu Projesi; Abbreviation: GAP)

National Irrigation Water Quality Criteria

Quality Criteria	Quality Classes of Irrigation Water				
	Class I (Perfect)	Class II (Satisfactory)	Class III (Usable)	Class IV (Usable with Care)	Class V (Improper, harmful)
EC_2 (microbes at 25 °C) x 10^6	0-250	250-750	750-2000	2000-3000	> 3000
Sodium (Na %)	<20	20-40	40-60	60-80	>80
Sodium Adsorption Ratio (SAR)	<10	10-18	18-26	> 26	
Residual Sodium Carbonate (RSC), meq/l	>1.25 <66	1.25-2.5 66-133	>2.5 >133		
Chloride (Cl), meq/l or mg/l	0-4 0-142	4-7 142-249	7-12 249-426	12-20 426-710	>20 >710
Sulphate (SO_4), meq/l or mg/l	0-4 0-192	4-7 192-336	7-12 336-575	12-20 575-960	>20 >960
Total Salt Concentration, mg/l	0-175	175-525	525-1400	1400-2100	> 2100
Boron Concentration, mg/l	0-0.5	0.5-1.12	1.12-2.0	>2.0	-
NO_3-N or NH_4-N, mg/l	0-5	5-10	10-30	30-50	>50
Fecal Coliform** 1100 ml, (CFU in 100 ml)	0-2	2-20	20-100	100-1000	> 1000
BOD_5, mg/l	0-25	25-50	50-100	100-200	>200
TSS, mg/l	20	30	45	60	>100
Ph	6.5-8.5	6.5-8.5	6.5-8.5	6.5-9	<6 or >9
Temperature, °C	30	30	35	40	>40

Selected UWWTPs

- 21 plants are initially selected to determine their treatment performance, composite sampling from influent and effluent, details of design and operational problems, comparison of the effluent with the irrigation water quality criteria,
- 4 extra UWWTPs, properly operating with no major problem are then selected for more detailed composite sampling & analysis on the performance (32 water quality parameters), comparison of the effluent with the irrigation water quality criteria,

Comparison of the Analysis Results of Selected UWWTPs Effluent with National Irrigation Water Quality Criteria

Plant name	Comparison of the Analysis Results of Selected UWWTPs with the National Irrigation Water Quality Criteria				
	SAR	Fecal coliform (CFU/100 ml)	Boron (µg/l)	Conductivity (µS.cm)	Cl^- (mg/l)
Afyon-Centre	41,9 (IV)	43 200 (V)	0,400 (I)	1 650 (III)	202 (II)
Bursa-Inegöl	119,4 (IV)	14 500 (V)	0,220 (I)	2 200 (IV)	925 (III)
Istanbul- Terkos	4,2 (I)	5 (II)	0,140 (I)	620 (II)	45 (I)
Istanbul-Paşaköy	12,7 (II)	3 500 (V)	0,570 (II)	825 (III)	95 (I)
Istanbul-Tuzla	113,4 (IV)	12 000 (V)	0,700 (II)	9 250 (V)	2 990 (V)
Istanbul-Ataköy	35,5 (IV)	5 000 (V)	0,500 (II)	1 700 (III)	410 (IV)
Muğla-Bodrum Centre	108,3 (IV)	0 (I)	0,865 (II)	7 380 (V)	2 380 (V)
Muğla- Bodrum Bitez	168,9 (IV)	9 600 (V)	0,650 (II)	13 000 (V)	3 740 (V)
Muğla- Bodrum Göktürkbükü	64,9 (IV)	300 (IV)	0,500 (I)	2 500 (IV)	690 (IV)
Düzce-Centre	16,7 (II)	27 000 (V)	0,470 (I)	700 (II)	98 (I)

Comparison of the Analysis Results of Selected UWWTPs Effluent with National Irrigation Water Quality Criteria

Plant name	Comparison of the Analysis Results of Selected UWWTPs with the National Irrigation Water Quality Criteria				
	SAR	Fecal coliform (CFU/100 ml)	Boron (µg/l)	Conductivity (µS.cm)	Cl^- (mg/l)
Izmir-Centre	70,1 (IV)	0 (I)	1,180 (II)	8 590 (V)	3 276 (V)
Izmir-Karaburun, Iskele	24,9 (III)	17 000 (V)	0,250 (I)	1 650 (III)	260 (III)
Sakarya-Centre	12,9 (II)	26 000 (V)	0,280 (I)	800 (III)	97 (I)
Isparta-Centre	23,6 (III)	28 800 (V)	0,450 (I)	1 125 (III)	110 (I)
Manisa-Akhisar	24,6 (III)	1 000 000 (V)	0,035 (I)	1 902 (III)	472 (IV)
Manisa-Alaşehir	24,6 (III)	1 000 000 (V)	0,055 (I)	1 289 (III)	69 (I)
Manisa-Centre	7,8 (I)	1 000 000 (V)	0,028 (I)	1 119 (III)	76 (I)
Aydin-Nazilli	14,5 (III)	1 000 000 (V)	0,066 (I)	1 764 (III)	127 (I)
Antalya-Manavgat, Kumköy	11,5 (II)	1 000 000 (V)	0,042 (I)	1 074 (III)	132 (I)
Antalya-Tikveyengöl	12,0 (II)	1 000 000 (V)	0,036 (I)	745 (III)	195 (II)
Kütahya-Centre	4,7 (I)	1 000 000 (V)	0,043 (I)	941 (III)	44 (I)

Comparison of the Analysis Results of Selected UWWTPs Effluent with National Irrigation Water Quality Criteria

Parameter	Silivri-Istanbul	Pasakoy-Istanbul	Kayseri	Adana
pH	6.95 (I)	6.92 (I)	7.4 (I)	7.55 (I)
BOD_5, mg/l	30 (II)	15 (I)	25 (I)	15 (I)
TSS, mg/l	25 (II)	30 (II)	20 (I)	7 (I)
TDS, mg/l	953 (III)	600 (III)	760 (III)	600 (III)
NO_3-N, mg/l	39.5 (IV)	27.5 (III)	8.1 (II)	10.05 (II)
SAR	31.6 (IV)	17.93 (II)	26.89 (IV)	11.54 (II)
Cl^-, mg/l	257 (III)	110 (I)	182 (II)	175 (II)
SO_4^{-2}, mg/l	118 (I)	110 (I)	125 (I)	106 (I)
EC_w, µS/cm	1588 (III)	1090 (III)	900 (III)	987 (III)
B, mg/l	<0.05 (I)	<0.05 (I)	<0.05 (I)	<0.05 (I)
F. Coliform, CFU/100 ml	4600 (V)	6000 (V)	600 (IV)	11×10^3 (V)

The effluent heavy metal concentration of the 4 selected UWWTPs regarding their suitability for irrigation according to national irrigation water quality criteria

Parameter	Silivri-Istanbul	Pasakoy-Istanbul	Kayseri	Adana
Boron, mg/l	<0.05 (S)	<0.05 (S)	<0.05 (S)	<0.05 (S)
Cd, mg/l	<0.02 (S)	<0.02 (S)	<0.02 (S)	<0.02 (S)
Cr, mg/l	<0.02 (S)	<0.02 (S)	<0.02 (S)	<0.02 (S)
Fe, mg/l	0.102 (S)	0.258 (S)	0.138 (S)	0.042 (S)
Pb, mg/l	<0.1 (S)	<0.1 (S)	<0.1 (S)	<0.1 (S)
Ni, mg/l	<0.05 (S)	<0.05 (S)	0.19 (S)	<0.05 (S)
Zn, mg/l	0.058 (S)	0.072 (S)	0.141 (S)	0.03 (S)

CONCLUDING REMARKS
Data Gathering on UWWTPs

- The required data and information were highly scattered among the State Authorities and not gathered from a single organization.
- Besides, some of the data have to be estimated based on literature survey and personal contact with the related governmental personnel.
- Part of the data necessitate confirmation and are considered to be less reliable.
- Proper recordings of data still lack and needs formation of a systematic database that can easily be accomplished even by public.

Concluding Remarks
Reuse Applications in Agriculture

- **The effluents of the selected UWWTPs are not suitable for agricultural irrigation purposes due to at least one significant water quality parameter that is the fecal coliform.**
- **Some of the plants do not even have disinfection units as their final polishing treatment stage.**
- **Satisfactory and efficient operation is rarely achieved due to high energy consumption and disinfecting chemicals requirement.**
- **Even though the national irrigation water criteria has been active since 1991, reuse of treated wastewater for irrigation has not been considered consciously till now as the country has not yet experienced severe water shortages.**

Concluding Remarks
Reuse Applications in Agriculture

- The farmers need to be informed on the safe use of effluents in irrigation is possible with serious control and monitoring of the effluent quality.
- Public awareness and training is another important issue that should be considered by the legal local or governmental related authorities.

Recommendations

- Infrastructure developments should be immediately involved in the databank and all the obtainable information must be up-dated.
- There is an imbalance in population distribution of the country, making the water and wastewater issues a difficult task.
- Most of the population is settled around the coasts of the country and the highly industrialized regions due to climatic conditions, geographical structure, existence of transportation network, fertility of land, and political aspects.

Recommendations

- Sustainable wastewater management can be promoted unless the existing situation is well defined.
- It also necessitates the investigation of the national monitoring and control acts, as without an idea on the national water and wastewater policies, it is very difficult to establish a healthy and satisfactory management strategy.

Reuse of Effluent in Irrigation, Spain (Vitoria)

Reuse of Effluent in Irrigation, Spain (Vitoria)

BIWA Lake- Japan

BIWA Lake- Japan

BIWA Lake- Japan

BIWA Lake- Japan

Thanks for your attention !

MEDAWARE- ITU Project Team

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WATER SAVING, REUSE AND RECYCLING IN INDUSTRY: CLEANER PRODUCTION OPPORTUNITIES

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Abstract

Natural resources include both the raw materials necessary for most human activities and the different environmental media, such as air, water and soil, which sustain life on our planet. Therefore, careful management of the use of these resources is a basis for sustainable development.

In contrast with raw material it is their declining quality that causes concern. It is not question of how much there is, but what state they are in.

Resource efficiency or resource productivity can be defined as the efficiency with which we use energy and materials throughout the economy, i.e. the value added per unit of resource input. An example of resource productivity calculation on a national level is total material (water) use divided by the total economic activity by the country, expressed in GDP.

Sustainable development calls for processes with a closed loop philosophy and in recycling becomes thus a normal, rather than exceptional solution. Water reuse and recycling in industry is one of the most important ways enabling absolute and relative decoupling of environmental impact from economic growth. There are more and more corporations focusing development efforts on Cleaner Production (CP) methods, i.e. systematic approach to using resource more efficiently, and avoiding the use of hazardous substances where substitutes are available.

Paper deals with water saving, reuse and recycling in Lithuanian industrial companies by Cleaner Production strategy, which is achieved by applying know-how, by improving technology and/or by changing attitudes. Cleaner Production strategy included the following prevention methods: good housekeeping, input substitution, better process control, equipment modification, technology change, product modification and on-site recovery/reuse.

In Lithuania CP strategy was introduced in 1993. Since then twelve Cleaner Production programmes have been implemented in different economic sectors (three CP programmes were integrated with implementation of environmental management systems). The results of water saving and reuse by applying CP methods from 120 companies, representing15 branches of industry are presented in the paper.

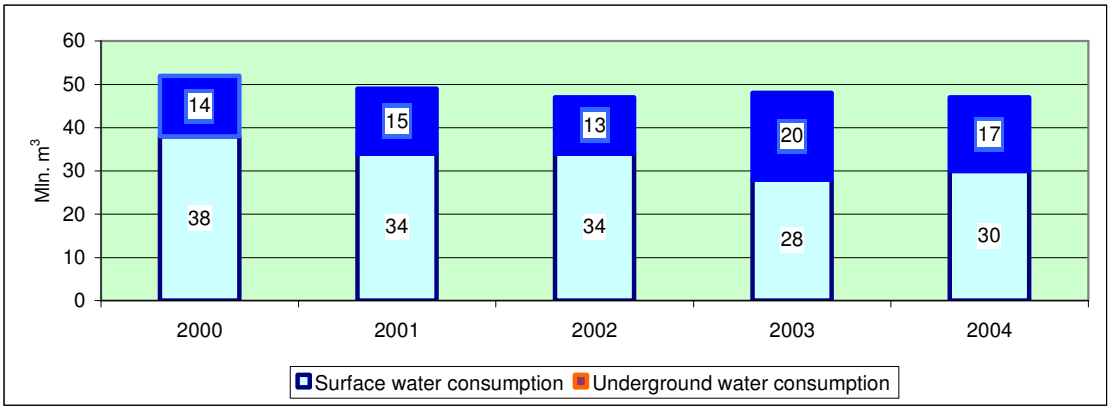

Fig. 1. Water consumption in Lithuanian industry

Fig. 1 shows, that despite of fast economic growth (GDP increased by 28% during the last three years), water consumption remains stable. This means that Lithuanian economy grows at a faster rate than environmental impact and relative decoupling was achieved mainly by using Cleaner Production opportunities.

Keywords: Cleaner production, sustainable industrial development, water saving, reuse, recycling

Water Saving, Reuse and Recycling in Industry: Cleaner Production Opportunities
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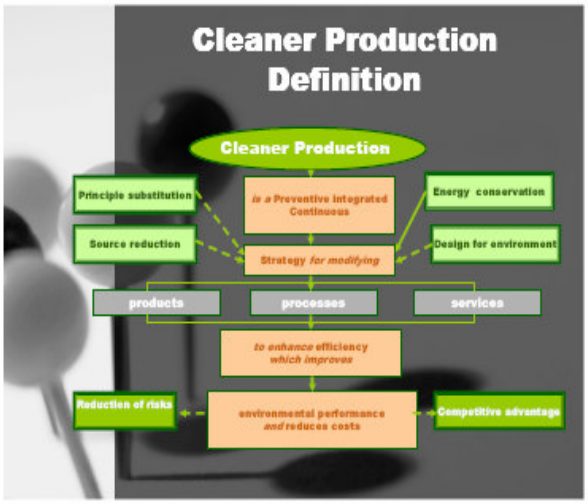
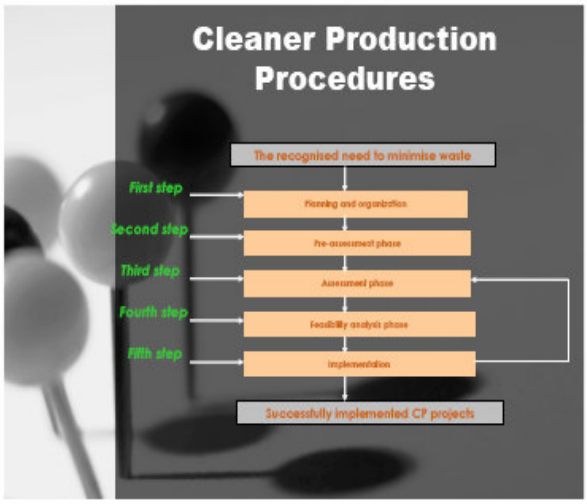
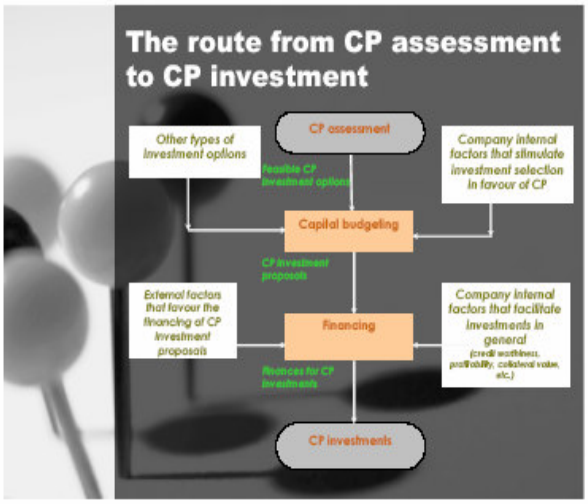
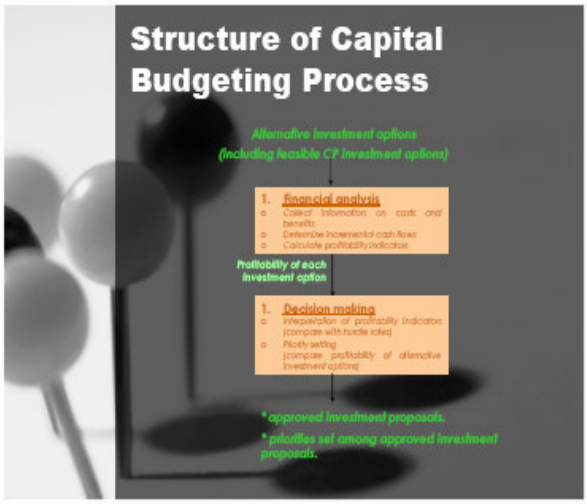
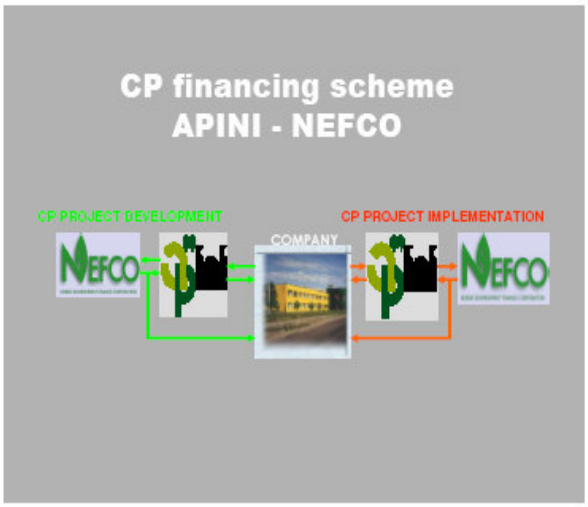

Cleaner Production Definition
Cleaner Production
Principle substitution
is a Preventive Integrated Continuous
Energy conservation
Source reduction
Strategy for modifying
Design for environment
products
processes
services
to enhance efficiency which improves
Reduction of risks
environmental performance and reduces costs
Competitive advantage

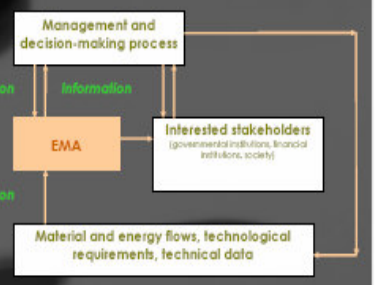

Cleaner Production Procedures
The recognised need to minimise waste
First step
Planning and organization
Second step
Pre-assessment phase
Third step
Assessment phase
Fourth step
Feasibility analysis phase
Fifth step
Implementation
Successfully implemented CP projects


The route from CP assessment to CP investment
Other types of investment options
CP assessment
Company internal factors that stimulate investment selection in favour of CP
Feasible CP investment options
Capital budgeting
CP investment proposals
External factors that favour the financing of CP investment proposals
Financing
Company internal factors that facilitate investments in general
(credit worthiness, profitability, collateral value, etc.)
Finances for CP investments
CP investments


Structure of Capital Budgeting Process
Alternative investment options
(including feasible CP investment options)
1. Financial analysis
Profitability of each investment option
1. Decision making
* approved investment proposals.
* priorities set among approved investment proposals.


CP financing scheme
APINI - NEFCO
CP PROJECT DEVELOPMENT
CP PROJECT IMPLEMENTATION
COMPANY
NEFCO
NEFCO

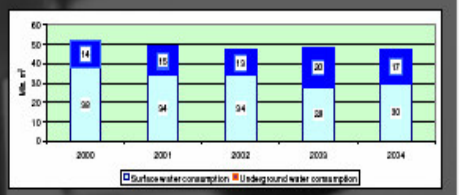
The Role of EMA in Decision-Making Process



Environmental benefits of implemented sustainable development measures in Lithuanian industry

Number of companies	71
Number of implemented innovations	151
Environmental results (yearly):	
EL Energy consumption reduced	27 584 000 kWh
Heat Energy consumption reduced	60 518 000 kWh
Waste amount reduced	86 700 t
Chemicals consumption reduced	850 t
Air emission reduced	79 500 t
Drinking water consumption reduced	*297 500 m³*
Diesel consumption reduced	387 000 t
Natural gas consumption reduced	5 883 000 m³
Fuel consumption reduced	656 800 t
Wastewater amount reduced	*622 500 m³*
Industrial water consumption reduced	*466 000 m³*

Water consumption in Lithuanian industry



Example 1
Implementation of control system for dying process and water consumption

Technical evaluation

- Inaccurate reiteration of colours for the same principles of prescription;
- deviations from technological requirements due to weak technological process control,
- overconsumption of technical water and steam,
- problem of redyeings and additional usage of energy resources, dyes and chemicals due to it, occurred during the material dyeing process.

It was decided to implement automatic control system for dyeing process and water consumption after technical, economical and environmental evaluation. The computerised control system will provide a possibility to control all the processes in the dyeing department. It will be possible to analyse parameters of each dyeing machine.

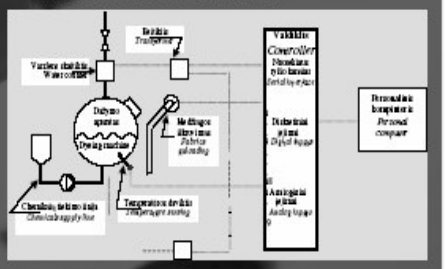
Economical effect

- Amount of redyes reduced by 10%;
- Consumption of dyes and chemicals reduced by 0,5%.
- Total investments - 25 226 EUR;
- Yearly savings - 27630 EUR;
- Pay-back period - 10 months.

Example 1
Implementation of control system for dying process and water consumption

Environmental benefit

Emissions to the atmosphere reduced by 0,17 t/year;
Electrical energy consumption reduced by 14 500 kWh/year
Steam consumption reduced by 115 Gcal;
Water consumption reduced by 5 060 m³/year;



Example 2
Recycling of water and oil in wet spinning process

Technical evaluation

Wet spinning machines must be flushed 8 - 10 times per shift. 21 000 m³ of technical water is used for machine flushing. The rings of wet spinning machines are regularly lubricated by oil. 34 tonns of lubricant are used annually.

Wastewater, contaminated by oil and yarn goes to the local wastewater treatment facilities.

The cleaner production project's aim is to reuse water and oil in the wet spinning process.

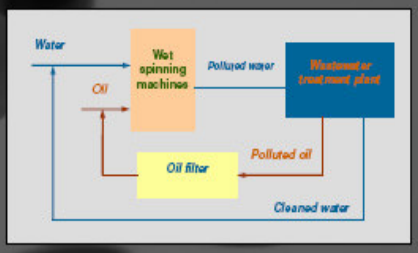
Environmental benefit

- ***Water consumption will decrease 19 500 m³/year;***
- Oil consumption will decreases 30.15 t/year;
- Higher quality of discharged water:
- BOD7 - 9.7 t/year;
- suspended solids - 9.7 t/year;
- oil - 0.019 t/year;
- fats - 0.97 t/year.

Economical effect

- Total investments – 32 232 EUR;
- Project annual savings – 32 858 EUR;
- Pay-back period - 1 year.

Example 2
Recycling of water and oil in wet spinning process



Example 3
Reconstruction of oxidation – phosphatation line in galvanic department

Technical evaluation

Old fashion galvanic baths with steam heating are changed into new stainless galvanic baths with electric heating system. The rinsing baths are equipped with Conductivity controllers that allow to control concentration of the solutions and to add fresh water only when the concentration exceeds allowed level. Installation of water recycling system with erlitic pumps allows to return water into the primary rinsing baths for secondary use.

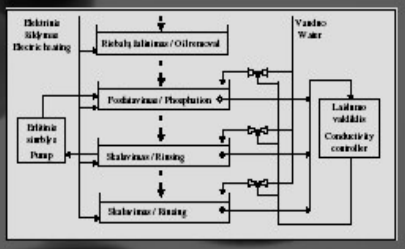
Environmental benefit

- 1 928 MWh of energy is saved;
- emissions into the atmosphere reduced by 7,85 t;
- galvanic sludge amount reduced by 1,35 t;
- Consumption of chemical materials reduced by 2,8 t;
- ***water consumption and wastewater discharge reduced by 1 130 m³;***
- grease amount reduced by 0,04 t.

Economical effect

- Project costs – 78200 EUR;
- Project's annual savings - 28255 EUR;
- Pay-back period - 2,77 years.

Example 3
Reconstruction of oxidation – phosphatation line in galvanic department



EFFICIENT MANAGEMENT OF WASTEWATER, ITS TREATMENT AND REUSE IN THE MEDITERRANEAN COUNTRIES - EMWATER

Göksel Akçin

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Abstract

Water shortage is currently one of the biggest concerns of human being worldwide and it becomes a global problem that affects seriously the lives of high numbers of the world population. The Mediterranean region belongs to the most affected countries in the world.

The primary outcome of the project will be to install and to increase efficiency and effectiveness in the management of wastewater, its treatment and reuse in Turkey, Jordan, Lebanon and Palestine.

The EMWATER partners' aim is to create awareness of innovative solutions in wastewater treatment and its reuse and support the installation of new technologies of wastewater management. Experts from the field, decision-makers and interested citizens and civil organizations have to be involved to reduce the water shortages in the Mediterranean Region. The responsibilities of the Mediterranean partner countries are the implementation of the results of the project and the transfer into actions as part of their water policies and strategies.

The responsibilities of the European partners are to work jointly with the Mediterranean partners to achieve the objectives of this project. These are know-how transfer of water especially wastewater treatment and reuse, to strengthen the capacity building, to assist the partner countries in the design and the construction of pilot plants for research and demonstration purposes and in the elaboration of policy guidelines.

The EMWATER project has set the following general objectives:

- Strengthening long-term regional co-operation and sustainable development in the Mediterranean countries.
- Improving efficiency and effectiveness in integrated water resource management.
- Promoting transfer of innovative wastewater treatment technologies and improving current technologies used in rural areas.
- Encouraging reuse-oriented wastewater management.
- Enhancing public awareness of the insufficient respectively wrong wastewater treatment and reuse and for the necessity of an improved hygienically safe disposal.
- Providing decision-makers with up-to-date, relevant information in order to help them choosing the most suitable technology.
- Exchange of experiences and know-how between the European and Mediterranean partner countries and among the Mediterranean partner countries.

The general objectives will be complemented by the following tasks:

- Elaboration of regional policy Guidelines for wastewater treatment and reuse.

- Adapted training and capacity building programs for technicians, engineers and employees of authorities and non-government
- Organizations in the field of wastewater treatment and reuse.
- Design and construction of pilot plants for demonstration and training purposes.

Though the project is limited in time to 48 months, starting in 2003 and ending in 2007, the measures it aims to implement are designed to create long-term, positive effects in the region.

"Efficient Management of Wastewater, its Treatment and Reuse in the Mediterranean Countries"

EMWater project

www.emwater.org

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This Project is funded by the European Union

Overview:

2003 – 2007

- MEDA Programme
- Euro-Mediterranean Water Network
- EMWater project objectives
- Activities of EMWater Project
- Introduction of InWEnt
- Training Programmes
- Wastewater Treatment System
- Pilot Plants
- Conclusions

NATO-CCMS Meeting 7-12 May, 2006 ISTANBUL

MEDA Programme

- In 1995 the European Union has started the MEDA Programme (Euro-Mediterranean Partnership)
- The Programme shall improve the infrastructure in the so called MEDA Countries
- Objective is the establishment of the Euro-Mediterranean Free-Trade Area in 2010

Euro-Mediterranean Water Network

- Important Milestone in this process has been the establishment of the Euro-Mediterranean Water Network in 1999
- The Euro-Mediterranean Water Network shall strengthen the regional cooperation between the MEDA Countries in the field of water supply and wastewater management

Water in the Middle East

- Water is an essential element for the economic development and political stability in the whole region
- Limited water resources are recognised as the most important obstacle to the development of the agricultural sector
- Aspects of decentralisation and privatisation are increasingly taken in consideration to enhance the efficiency of water management

Activities of EMWater Project

Implemented Activities 2003 – 2007

- Training needs Analysis
- Country studies Conducted and Published
- Training Programs for each years
- Design and Construction of Pilot Plants

Objectives of the EMWater Project

Efficient Management of Wastewater Treatment and Reuse in the MEDA Countries is increased

- Development Policy Guidelines
- Human Resource Development
- Development of appropriate Technologies
- Design and Constuction of Pilot Plants
- Capacity Building Program
- Conduction of Country Studies

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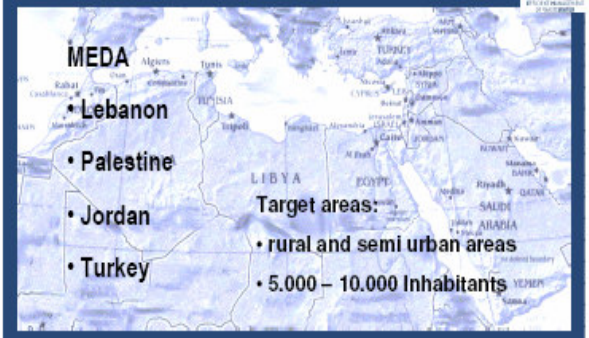
Target Countries/Target Areas



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Partners

Europe

- InWEnt Capacity Building International, Berlin Germany
- Adelphi Research Berlin Germany
- TUHH, Hamburg Germany
- ENEA, Bologna Italy

MEDA

- American Lebanese University, Byblos Lebanon
- University of Balamand, Tripoli Lebanon
- YILDIZ Technical University, Istanbul Turkey
- Birzeit University, Birzeit Palestine
- Al al Bayt University, Al Mafraq Jordan

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InWEnt:

Internationale Weiterbildung und Entwicklung gGmbH

"Capacity Building International, Germany"

Merger between
Carl Duisberg Gesellschaft (CDG)
and
German Foundation for International Development (DSE)
in 2002

A German governmental organization for international capacity building and sustainable development

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Business Fields of InWEnt

- Domestic political Information in Germany
- International dialogue and exchange of experience
- Qualification of experts from developing Countries
- Qualifications of German/EU professionals in Germany/EU
- Preparing of German experts for their foreign assignment for the German Development cooperation

More than 35.000 participants every year

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NATO-CCMS 7-12 May, 2006 ISTANBUL

Procedure for Preparation and Implementation of the Training Program 2003-2004

- Training needs assessment summer 03
- Approvement from MEDA Partners on the local * SC
- Development of training schedule/plan
- Announcement/ advertisement in different media
- Selection of participants/ trainers by local partners and local SC
- Implementation of the TC June 04 - Dec. 04
- Evaluation

*SC: Steering commitees

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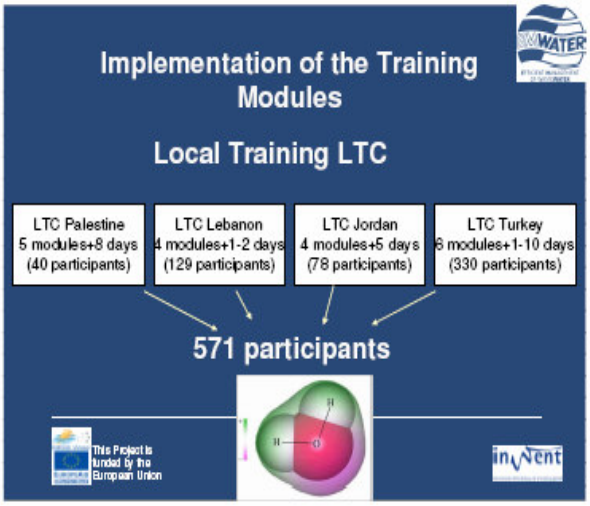
participants selection:
leading position
Experience


Implementation of the Training Modules
Local Training LTC
LTC Palestine
5 modules+8 days
(40 participants)
LTC Lebanon
4 modules+1-2 days
(129 participants)
LTC Jordan
4 modules+5 days
(78 participants)
LTC Turkey
6 modules+1-10 days
(330 participants)
571 participants
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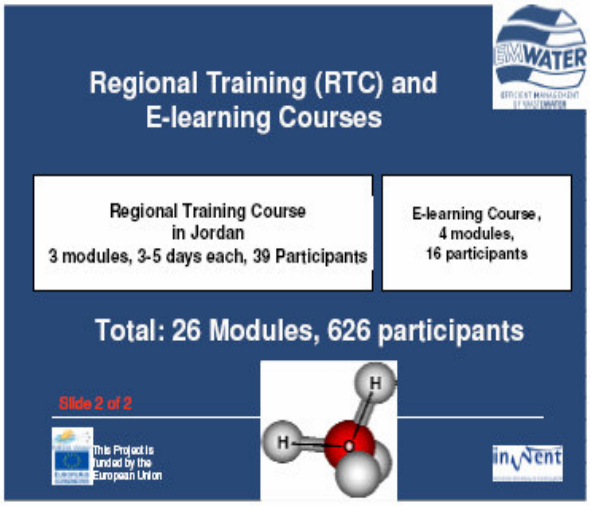
Regional Training (RTC) and E-learning Courses
Regional Training Course in Jordan
3 modules, 3-5 days each, 39 Participants
E-learning Course,
4 modules,
16 participants
Total: 26 Modules, 626 participants
Slide 2 of 2
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European Union

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Results of the Training Program

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Training Modules (June 04 – Dec. 04)

Modules	Jordan	Lebanon	Turkey	Palestine	Duration/ Trainers and Experts
➢Wastewater and low-cost technology	x	x	x	x	2-5 days, local/EU
➢Wastewater Quality Control	x	-	-	x	5 days, local
➢Environ-mental impact assessment	x	-	-	-	5 days, local
➢Efficient Management of wastewater treatment and reuse projects	x	x	x	x	1-5 days local/EU
➢Development of policy guidelines	x	x	x	x	1 day interactive workshop
➢Institutional and project Managment	-	-	-	x	5 days, local
➢Awareness campaign	-	x	x	-	1 day, local
➢Round table on WWT/reuse	-	-	x	-	3 days, local
➢Wastewater training for Schools	-	-	x	-	7 days, local

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Training Modules (June 04 – Dec. 04)

Modules	Jordan	Lebanon	Turkey	Palestine	Duration/ Trainers and Experts
➢Wastewater treatment for rural managers and decision-makers	-	-	x	-	1-4 days, local/EU
➢Operation and maintenance of wastewater treatment plants	x	x	x	x	1-10 days, local/EU
➢Planning and design of WWTP	x	x	x	x	1-5 days, local/EU
➢Wastewater management in rural and suburban areas	x	x	x	x	1-5 days, local/EU
➢E-learning: ➢- Wastewater characterstics ➢- Sustainabe concepts ➢- Economic aspects ➢- Construction and design of WWTP ➢- Wastewater reuse	x	x	x	x	40 hours/TUHH

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Number and Distribution of Participants

Country	Male	Female	Total	Institution		
				Public	Private	Position/ Qualification
Jordan	61	17	78	66	12	Municipality WW-Engineers/Civil Engineers
Palestine	26	14	40	27	13	Municipality WW-Engineers/Civil Engineers
Lebanon	98	31	129	61	68	Municipality WW-Engineers/Civil Engineers
Turkey	185	145	330	261	69	Municipality WW-Engineers/Decision-makers/Ministries/ Schools

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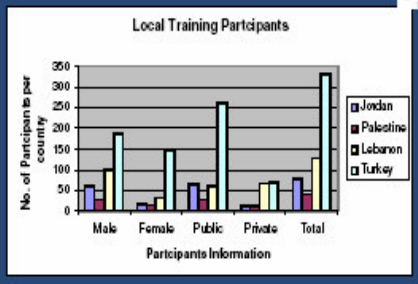
Local Training Participants



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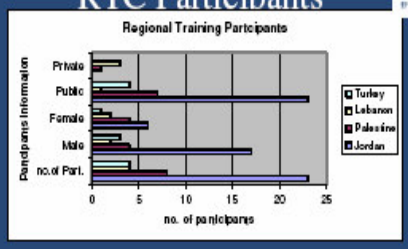
RTC Participants



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TRAINING PROGRAMMES 2005

- Training Course No1: 5 working days, 07-11 November 2005.
- Efficient Management of wastewater treatment (planning and design of WWTP, operation and maintenance with focus on trouble shooting, treatment technologies and privatization).

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- Training Course No2: 7 working days, from 14-18 November and 21-22 November 2005.
- Efficient management of wastewater reuse (management, regulation/ standards, impact on soil, hygienic aspects, economic aspects).
- Training Course No3: 8 working days, 23-25November and 28 November-02 December 2005.
- Low-cost and appropriate technology of wastewater treatment (small-scale wastewater treatment plants and ecological sanitation).

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- Training Course No. 4: 5 working days, from 05 December-09 December 2005.

Socioeconomics, environmental aspect, and public awareness of wastewater treatment.

NATO-CCMS 7-12 May,2006 Istanbul

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EVALUATION OF LTC 3rd YEAR 2005

No of LTC	Number of Participants	Number of Female	Number of Male
1T	43	30	13
2T	30	22	8
3T	30	22	8
4T	22	19	3
Total	125		
From YTU	111		
From NGOs	14		

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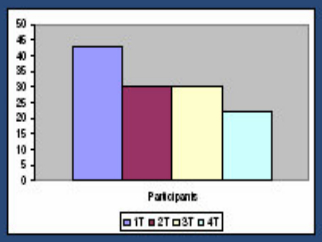
Summary of the Evaluation Results Participant Numbers



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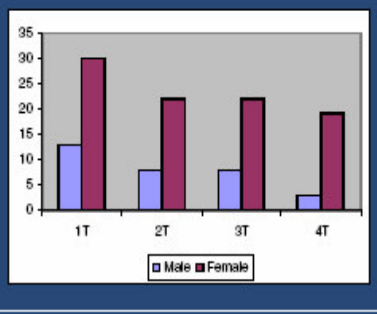
Summary of the Evaluation Results



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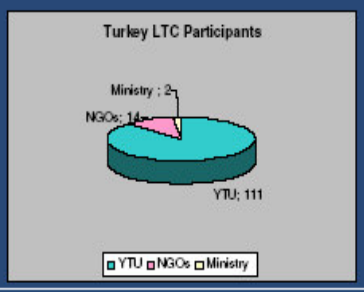
Participants numbers attended the training courses were distributed as follows:



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Conclusion and Suggestion for Future Training Courses

2005

- 125 Participants attended the LTC (quite good number of women)
- Trainers all local.
- Good involvement of stakeholders by the design of the training program
-
- Different Topics were proposed by the traineeer to be covered in future training especially WWTP operation and Maintenance

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Disseminations

- I presented our project in YTU EU Office that was on 18 October 2005 most of the participants were EU Delegations YTU and some steakholders.
- I presented our project in EMWIS Seminar that was on 15 Dec.,2005 in ANKARA.
- I presented our project in ITU on 24 January 2006.
- I presented our project in Spain 20 February 2006.

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- Pilot Plants in MEDA Countries

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Design and Construction of the Pilot Plants Lebanon and Jordan

Country	Treatment Technology	Details of Treatment
Lebanon 2 x pp	Contact Stabilization Sludge	Aeration 1 - 24 → Screening Tank Gravel Steel → Balancing Tank → Contact Aeration Tank → Setting Tank → Chlori-nation → Sand Filter → Active Carbon Filters-Reuse Purposes; Setting Tank → Sludge Re-aeration → Sludge Aerobic Digester → Aeration 1 - 24
Jordan 1 x pp	Activated Sludge Treatment	Sanitary sewer network → Screening Unit → Biological Treatment (Pre-Denitri-fication → Aeration) → Sludge stabi-lization tank → Filtration tank (Rapid filter 15 m³/m² / Option: Wetland filtration) → Chlori-nation (Option: UV-light) → Irrigation tank

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Design and Construction of the Pilot Plants Turkey and Palestine

Country	Treatment Technology	Details of Treatment
Turkey 1 x pp	Anaerobic Baffled Reactor Followed by Rotating Biological Reactor (ABR – RBC)	*UASB Principle ABR Reactor → RBC Reactor → Settlement Tank → Tertiary Treatment Wetland – Reuse Purposes
Palestine 1 x pp	Ditto	Ditto → Tertiary Treatment Sand Filtration

UASB: Upflow Anaerobic Sludge Blanket

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THE WASTEWATER TREATMENT SYSTEM

In order to assess an appropriate treatment concept for the MEDA-countries and thus for the pilot plant in Turkey, an evaluation was performed as first step.

The following criteria were found to be most important for long term sustainability of water reuse concepts in suburban and rural areas of the MEDA countries:

- - Affordable; especially low operation costs
- - Operable; operation must be easily possible with locally available staff and support
- - Reliable; producing a safe effluent for water reuse
- - Environmentally sound; little sludge production and low energy consumption
- - Suitable in Mediterranean climate

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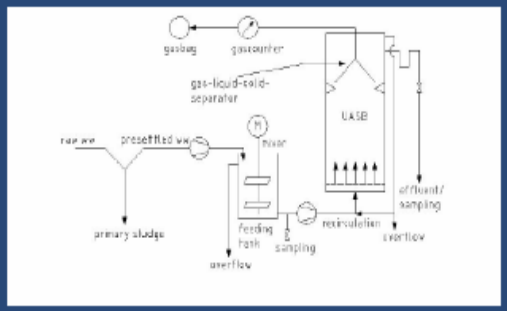
Scheme of the UASB reactor



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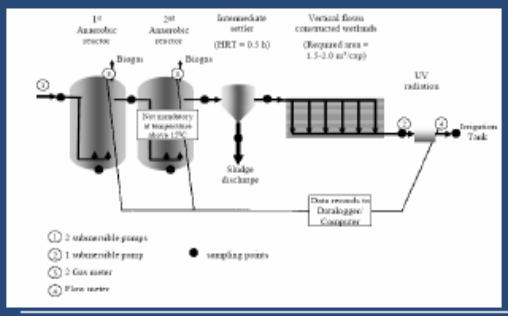
Treatment system for the pilot plant in Turkey



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- The treatment cycle as shown in figure was assessed to fulfill sound these criteria for the following reasons.
- The operation costs are very limited, consists mainly of pumping costs,
- No aeration is necessary which represents usually the major financial part. Maintenance can easily be done and educated to local staff.

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- As primary treatment, the anaerobic step provides physical as well as biological treatment with a very low sludge production, less than 10% of conventional systems with activated sludge.
- Sludges discharge is only necessary once or twice a year and can be applied on the fields according to agricultural needs. Depending on the ambient temperature, one or two high rate reactors, e.g. UASB are required.
- Reported that at a temperature of 15^{0}C an anaerobic filter followed by a UASB reactor is a suitable system for the treatment of domestic sewage.

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- As secondary treatment, constructed wetlands (CW) were chosen to be the basic unit. CW act as biofilters combining physical, chemical and biological treatment and are especially suitable for low diluted water flows as many plants prove.
- In the last years, vertical flow CW were developed in Europe which provide aerobic conditions due to intermittent feeding and a better performance than submerged beds or free water CW.

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- This treatment cycle is not designed to remove nutrients as for irrigation the nutrients like nitrogen, phosphorus and potassium can additionally fertilize the plants when applying the treated water on the fields.

  There are sufficient experiences and data available about the treatment performance of CW and UV radiation for municipal wastewater even in cold climate. But there is only limited research on the applicability of UASB reactors at moderate and cold temperature.

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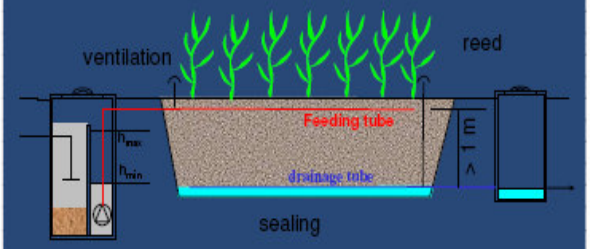
Constructed wetland - vertical view



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TUHH

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TUHH

Conclusions:

- Training program design was based on the specific situation in the MEDA countries: public awareness in Lebanon and Turkey, project management in Palestine, environment and effluent standards/irrigation standards in Jordan.
- Around 626 participants from the region have attended the training courses, target group mostly municipality wastewater engineers
- Trainers were mostly from the MEDA region. EU partners provided excellent support

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- We have got good involvement of stakeholders and NGOs in the planning of training courses
- Quite good number of females attended the training courses (25 – 30 %)
- Training courses were practical and interactive oriented
- There was a good mix between presence training courses and the online training
- Good experience exchange between experts in the MEDA countries through the regional training course and the online training has been achieved
- Started constrct wastewater pilot plant.

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15 Dec.,2005 EMWIS Seminer ANKARA

THANKS MY PARTNERS

- Claudia Wendland*, Joachim Behrendt*, Elmitwalli*, Ismail Al Baz**, and Ralf Otterpohl*
- * Institute of Wastewater Management, Hamburg University of Technology (TUHH), Germany
- ** InWEnt Capacity Building International, Amman, Jordan

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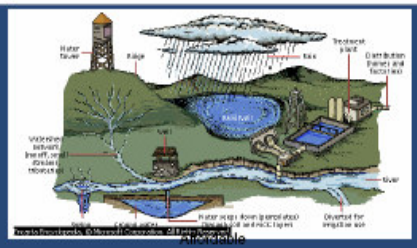

Thank you for your Attention

EMWater project

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Thank you/Teşekkür ederim

This Project is funded by the European Union

Prof. Dr. Göksel AKÇİN (Project Manager TURKEY)
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PROBLEMS AND APPLICATIONS OF WATER REUSE IN ISRAEL

Chaim Forgacs

The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva, Israel (forgacs@bgumail.bgu.ac.il)

Abstract

In Israel all the available water reserves are employed, and the increasing population and technological developments require every year additional amounts of water supplied to industry, agriculture and municipal needs.

Efforts are made to balance the increasing deficit with a variety of methods - water desalination, import of water (from Turkey) and water reuse and recycling.

Among the methods of water reuse and recycling to be discussed in the presentation are the use of secondary municipal effluents in agriculture, deep well injection of effluents, combined water utilization in industrial complexes and municipal use of grey water.

Problems and Applications of Water Reuse in Israel

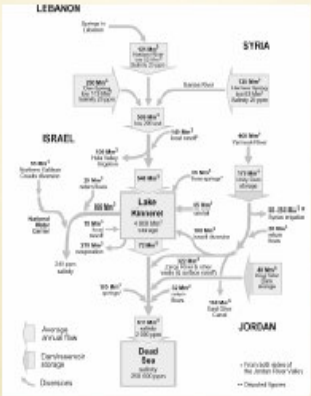
Chaim Forgacs, Israel

Abstract

- In Israel all the available water reserves are made use of, and the increasing population and technological developments require every year additional amounts of water supplied to industry, agriculture and municipal needs.Efforts are made to balance the increasing deficit with a variety of methods - water desalination, import of water (from Turkey) and water reuse and recycling.Among the methods of water reuse and recycling to be discussed in the presentation are the use of secondary municipal effluents in agriculture, deep well injection of effluents, combined water utilization in industrial complexes and municipal use of grey water.

- Israel has three immediate options to meet the problem of increasing water demand and irregular water supply. It can import water from Turkey, at a cost of 80 cents per cubic meter, it could desalinate seawater, at a cost of 52-55 cents per cubic meter, or recycle used water via wastewater processing plants, for 35 cents per cubic meter.

- # Utilization of surplus winter runoff. This water, collected in artificial seasonal lakes (110 built in the past decade), is used for irrigation and, when possible, for recharging of aquifers. The lakes also store treated effluent and water in transit from one region to another. Recharging of aquifers also helps prevent evaporation and, in the coastal area, intrusion of seawater. Once underground, the water is available for repumping as needed.
- # Re-use of treated household and industrial effluents. Estimated at 500 million m per year, this is the largest water source awaiting intensive development. More than one third of the quantity is used in agriculture today, mainly for cotton and fruit, crops, which do not lie directly on the soil. The rest is either recharged to groundwater or discharged into watercourses and the sea for lack of storage possibilities.
- # Desalination. Israel has some 30 desalination facilities today, mostly in the Eilat area. The largest uses reverse osmosis to treat 27,000 cubic meters per day of brackish water, thus meeting half of Eilat's needs. All available brackish water in the Eilat - Arava region is desalinated today. The future of desalination focuses on seawater as a source and depends on finding ways to make the process cost-efficient.
- # Rainfall enhancement. Seeding clouds with silver iodide crystals, carried out over the Lake Kinneret basin since 1974, has increased annual rainfall in the area by 15-18 percent. The World Meteorological Organization has cited the Israeli program as the only one worldwide, which statistically shows significant success.
- # Conservation. As the most reliable and least expensive way to stretch the country's water resources. The challenge is being met in all sectors.



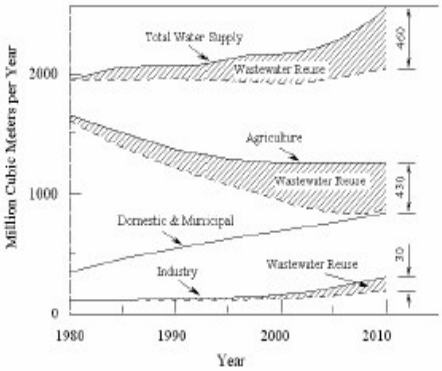


Table 1: Water Resources and Supply Balance in Israel

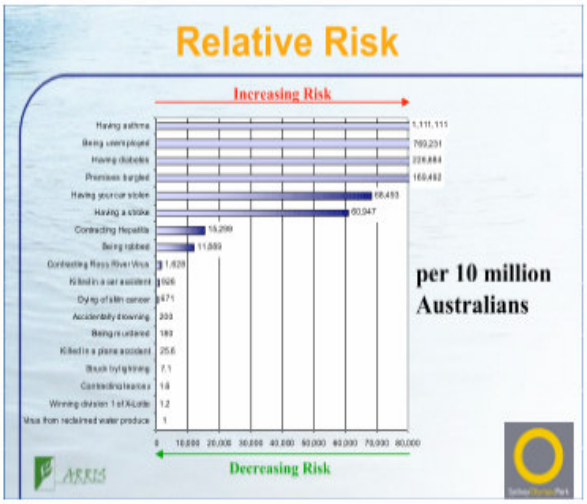
Hydrological year[1]	1985/86	1990/91[2]	1999/2000[3]	2010/11[3]
Water source	Million cubic meters per year (MCM/yr)			
Groundwater	1340	1140	1100	1100
Surface water (Jordan Watershed)	620	140	210	600
Floods impoundment	40	–	20	60
Desalination	–	–	10	230
Reused wastewater	110	190	285	460
Total production	2110	1470	1625	2450
System's losses	–60	–40	–40	–50
Total supply	2050	1430	1585	2400

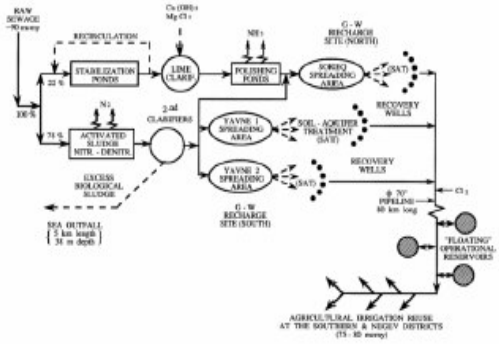
Hydrological year[1]	1985/86	1990/91[2]	1999/2000[3]	2010/11[3]
Water demand	Million cubic meters per year (MCM/yr)			
Municipal and Domestic	445	560	700	830
Industrial	115	120	165	280
Agricultural	1490	750	720	1190
Recreational	–	–	–	100
Total	2050	1430	1585	2400

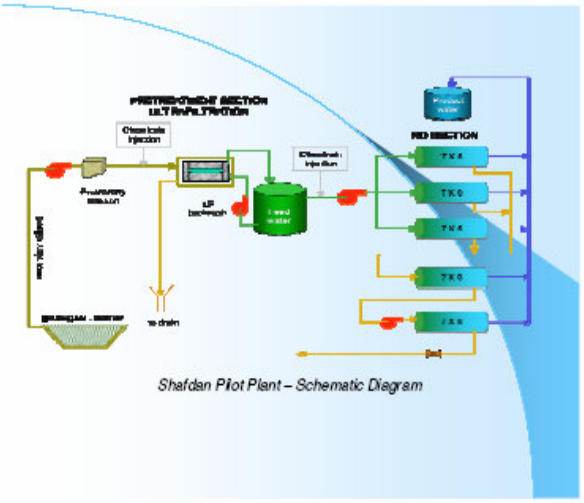
Hydrological year (Oct.-Sept.)	Total water supply	Agricultural supply	Reused Wastewater		
	MCM/yr	MCM/yr	MCM/yr	% of total supply	% of supply to agriculture
1985/86	2050	1490	80	3.9	5.4
1988/89	2050	1280	160	7.8	12.5
1990/91[1]	1430	750	190	13.3	25.3
1997/98	2040	1230	255	12.5	20.7
1999/00[1]	1585	720	285	18.0	39.6
2010/11[2]	2400	1190	430 [3,4]	17.9	36.1

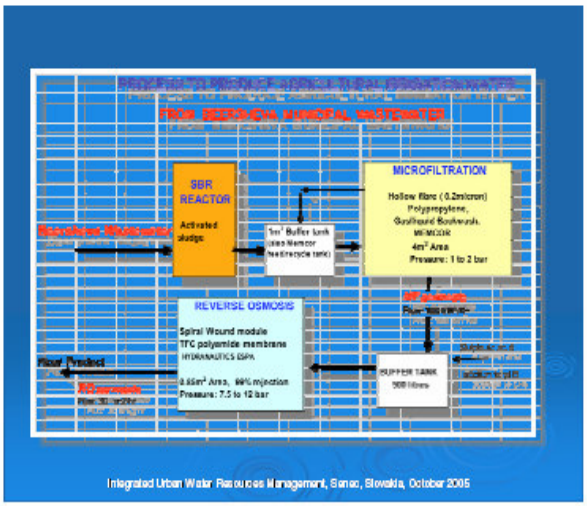
Typical characteristics of municipal wastewater in Israel

Parameter	Units	Typical range	Tel-Aviv	Haifa
BOD	mg/L	300-600	417	593
COD	mg/L	600-1800	1009	1360
TSS	mg/L	250-600	382	690
Chlorides	mg/L	120-500	300	412


Relative Risk
Increasing Risk
per 10 million Australians
Decreasing Risk




Shafdan Pilot Plant – Schematic Diagram


SBR REACTOR
Activated sludge
MICROFILTRATION
REVERSE OSMOSIS
Spiral Wound module
TFC polyamide membrane
Pressure: 7.5 to 12 bar
Integrated Urban Water Resources Management, Sanoc, Slovakia, October 2005

This is the Objective !

Table 1 : Performance of SBR & microfiltration treatment processes

	Influent	SBR effluent	MF effluent
pH	8.1 ± 0.2	8.0 ± 0.2	7.8 ± 0.2
Conductivity, mS/cm	1.7 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
TDS, mg/L	1150	1022	970
Alkalinity, mg/L $CaCO_3$	352 ± 50	215 ± 14	212 ± 20
BOD total, mg/L	245 ± 13	13.6 ± 7.7	3.7 ± 1.5
BOD filtered, mg/L	94 ± 2.9	3.6 ± 1.2	3.7 ± 1.5
COD total, mg/L	804 ± 154	77.31 ± 6.8	38 ± 6.1
COD filtered, mg/L	312 ± 22	44.2 ± 10.1	38 ± 6.1
DOC, mg/L	28.4 ± 0.1	12.0 ± 1.7	12.3 ± 1.9
NH_4, mg/L	40.3 ± 18.2	3.7 ± 4.4	3.7 ± 8.0
NO_3, mg/L	<1	41.8 ± 10.9	41.4 ± 11.3
NO_2, mg/L	<1	3.2 ± 2.9	3.5 ± 3.2
PO_4, mg/L	44.8 ± 23.9	54.6 ± 16.8	6.8 ± 17.1
TSS, mg/L	318 ± 78	17.5 ± 9.8	8
Turbidity, NTU	>300	7.2 ± 3.5	0.1 ± 0.03
Total coliforms, cfu/ml	$25 \cdot 10^6$	$8.6 \cdot 10^3$	40*
Fecal coliforms, cfu/ml	$5.4 \cdot 10^6$	$2.4 \cdot 10^3$	22*
Total count, cfu/ml	$8.3 \cdot 10^6$	$6.8 \cdot 10^5$	387*

(*)-spores are completely disinfected

CONCLUSIONS

The overall results of MF or UF treatment of secondary effluents indicate the feasibility of this operation.
This treatment resulted in BOD<5 mg/L, TSS<1 mg/L and turbidity<0.1 NTU. Bacterial counts showed 6-log removal of coliforms and fecal coliforms.

These results indicate that this treatment is capable of producing an effluent that meets or even surpasses the requirements for unrestricted water reuse for agriculture.

After disinfection, such effluents can easily meet the Israeli requirements for unlimited crop irrigation.

Acknowledgement

Information on membrane processes was provided by Dr. Rami Messalem

IMPROVING WATER QUALITY THROUGH LOW-COST UPGRADING OF A WATER TREATMENT FACILITY ACCOMPANIED BY ABANDONMENT OF CHLORINATION

William M. Zadorsky [1], **Boris V. Pismenny**[2]

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(
[2] *VOSTGOK Laboratory, Zholty Vody, Ukraine*

Abstract

The problem of pure drinking water is one of the sharpest for a lot of cities and of countries. Ways of a solving this problem are defined today not level of development of science and technology, as sufficiently efficient technologies for getting given quality drinking water are designed, but in greater degrees by financial possibilities of country on the modern water supply stations building and current it is costs payment on the usage of these stations. For developing and comparatively non-rich countries will possible turn out to be an interesting a work of Ukrainian experts, directed on creation for the cheap water preparing, ensuring under small capital embedding and field-performance expenses necessary quality of drinking water.

Condition practically of all sources of drinking water on the territory of Ukraine is so catastrophic, that represents by itself a threat of a survival of the population. While the water sources of the first category of quality should be used, the water in Dnieper on international standards have nearer to III-IV category of quality that is, its norms almost corresponds with the diluted drains. Existing water supply systems on the territory of Ukraine assume preliminary chlorine processing of initial water, which then processing by aluminium sulphate , updating pH by lime-milk, upholding, filtering of the top fuse, chlorine processing and submission of water to the consumer. Thus there occurs clearing of lambs and disinfecting of water with simultaneous by operating time chlorine-organic derivative. Radioactive elements, hard metals and chlorine-organic derivative practically free treat in the system of drinking water supply for the population.

The program of work on maintenance of the inhabitants of industrial city by qualitative drinking water including the use of new two step reagent technology of water preparation and its introduction without any reconstruction on acting water supplying plants, electrical pulsing and light disinfecting of water, creation of manufacture of local installations for disinfecting of water without chlorine processing.

Increasing water pH to 11 will result in deposition of magnesium hydroxide and calcium carbonate under certain conditions in a mixing/precipitation tank. More than 90 % of the heavy metals and radionuclides, over 80 % of the organic contaminants and all bacterial pollutants are removed in the process. The final step is water neutralisation with a hydrolysing coagulant (salt of aluminium or iron) for further purification. All additives are readily available. A mixing/precipitation tank is the only necessary addition to the existing equipment. The present practice allows to carry out a complex clearing of water from heavy metals, (Fe, Mn, Al, Be, Cu, As, Pb, Zn, Se, Cd, Ti, Ni, Hg, Cr etc.); radioactive elements, (U, Th, Pb-210, Po-210, Sr-90,.As-137, Ra-226); petroleum, pesticides, other organic inclusions with simultaneous water disinfecting without the application of chlorine and operating time of cancerogenous -organic derivatives. The level of water purification from this elements and combinations is from 92 to 98 percents, what is best in compare with traditional «chlorine» water purification technology in all municipal water treatment plants in the

former Soviet Union. It is possible to summarise the project results for spinning off to other areas in Ukraine and developing countries.

NATO COMMITTEE ON THE CHALLENGES TO MODERN SOCIETY

Clean Products & Processes Pilot Study

Istanbul, Turkey

May 7-12th, 2006

Systematic Approaches to Handling Ukrainian Water Problems

Prof. William Zadorsky

Ukrainian Ecological Academy of Sciences

- The environmental pollution in Ukraine has reached critical levels. Vehicles, power plants, steel mills and nonferrous metallurgy works are the major air polluters. Pesticides are responsible for much of the harm done to human health. Water pollution continues on a large scale. The Dnieper region is the worst affected among its counterparts in Ukraine. Here, the situation is disastrous because of a combination of energy-intensive industries, thermal power generation, and intensive agriculture, further aggravated by Chernobyl.

- Ecological conditions in Ukraine have become aggravated not only by the Chernobyl tragedy (recently we discussed the Chernobyl lessons as it was 20 years ago), but also by specific features of the region. This is described by a combination of an intensive agriculture with an intensive industry and with an advanced power system. It is difficult to overestimate the harmful influences on the environment.

- There is an urgent need to find feasible ways that would stop the ensuing depopulation in Ukraine, such ways to ensure survival that would work before the sustainable development concept has been implemented. In these times of a deep economic crisis, the economic and environment-related issues must be attacked simultaneously, in line with one strategy for a cleaner economy.

- It is not a report of ecological passions of Ukraine. Do not expect to find in my report series "how to survive ", any of "hot" figures about mortality, decrease of human life time or increase of defective children quantity which were born in our country. This report is to research the reasons and analyze our ecological problems and the prospects for their resolution.

- First of all this report is devoted to a problem of pure water, which for our country is one of sharpest. Condition practically of all sources of drinking water in Ukraine is so catastrophic, that represents by itself threat of a survival of the population.

- While it should be used the water sources of a first category of quality, the water in Dnieper on international standards have nearer to III-IV category of quality. Thus in quality the basic pollution the heavy metals and radio-nuclides, petroleum, phenols, pesticides, pathogenic micro-organisms are acting. Except natural radio-nuclides, which source are the deposits of uranium ores in territory of Ukraine, radio-Isotopes are present in water, that have got as the result of Chernobyl accident.

- Only recently Ukraine got status of country with a market economy and went out from number countries with a transitional economy. However the state is not enough controlled market economy of Ukraine while. As a results during restructuring and technical rearmament of productions in connection with the change of owners the most cheap variants of technologies are used, the cleanness of production does not rise, the most ecologically harmful products are made, the dangerous packing are used and etc.

- The problems of the Ukraine market economy influencing can be illustrated the examples of the Pridneprovie region, when ecologically dangerous enterprises and technologies are created in flagrant contradiction with the conception of sustainable development in order to please the requirements of the market. It is possible to name "chemical terrorism" without overstatement. Special attention has to be paid to the use in Ukraine of the "special" fuel on the base of wastes of coke factories, containing carcinogen benzene which concentration surpasses allowable one in the civilized world more than 20 times

- Only strategy of sustainable development and concept of cleaner production as its parts can resist to attack of the market. Nevertheless no cleaner economy will be possible without creating a civilized environmental market.
- The success of a cleaner economy policy will be largely determined by the availability of professionals well trained in the theory and practice of "economy clean-up" and environmental management.

These strategic principles determine some tactical measures that include:
- no waste due to improved selectivity,
- neutralizing wastes directly at the origin, rather than at the exit,
- flexible technologies,
- recycling materials and energy,
- conservation of resources,
- waste treatment, etc.

These tactics must be combined with certain design and engineering processes, such as
- providing a considerable excess of the least hazardous agent,
- minimizing dwell times,
- recirculation of materials and energy via closed loops,
- concurrent reactions and product separation,
- introduction of heterogeneous systems,
- adaptive processes and apparatuses,
- increasing throughputs,
- multifunctional environmental facilities, etc.

- As regards water problems of Ukraine it is necessary to use system analysis for its resolution. The typical hierarchy of levels (tiers) is below submitted.
- For each of levels the tools and methods of the water problem solving are corresponding to scale of this level (tier).
- Further I would like you to acquaint only with some from our "water" works at various levels of hierarchy.

№	Tier of Hierarhy	Concepts	Tools and methods for water handling. Samples	Optimization Parameters
1	Ukraine	Sustainable Development	Systematic Approach	Sustainability indexes
2	Region	Industrial - Agrarian Symbiosis	Pollution Prevention, Cleaner Production, Enterprises Restructuring, Use of active Silt from sewage treatment	Cost
3	City	Industrial Symbiosis	Optimization of water supply point, Drinking water PET bottling	Cost
4	Enterprise	Recycling, Local Waste Water Cleaning	Complex processing of activated sludge for agriculture	Quantity
5	House	Local cleaning of the leading in the house drinking water	Membrane processes	Quantity
6	Flat	Local cleaning of drinking water before flat entry	Management of consumer properties of water. Anodic, cathodic water	Quality
7	Inhabitant	Surviving concept	Ukrainian Program of Adaptation and rehabilitation of inhabitant to technogenous loads realization	Quality

1.Ukraine

- It is known, that Ukraine is one of least water supplied regions of Europe. The potential local resources of superficial and underground waters make 6O klm3, and specific parameter of water supplying expense of local water resources in Ukraine is one of lowest in former USSR (about 1000 m3 per one year for one inhabitant). The concentration of the harmful substances in water is raising from year to year.
- Symptomatically, that in the electronic atlas of the world " PC Globe 5.0 " Firms Brodrbund Software Inc., it is marked the water on Ukraine is not suitable for the use.

- Existing system of supply of the population of the drinking water generated on old FSU standard "Water drinking ", under condition of conformity of sources of water in Dnieper was of the first category of quality, but today water is indicated as third- fourth category of quality.

- Last years situation became even worse. Process of chlorine processing of water, used on all urban stations of water, supply is accompanied by formation carcinogenic chlorine-organic connections. So, only chloroform contents in near Dniepr region drinking water, on the data of laboratory of «Green Peace» organisation, exceeds limiting allowable norms in 2-5 times.

- We drink water from Dnieper, which at our water supply stations clear with guarantee only from dangerous micro-organisms. Here it is difficulty to blame of our water specialists. Why the water in Dnieper has become toxic? Who is guilty? What we have to do? Perpetual our Slavic questions...

- Already long time we accept, but never we executed, the state programs of clearing and saving of Dnepr and clearing of the small rivers. Canada and other countries try to help us.
- But a problem is that waters of Dnepr *cannot be cleared*, unless pollution ceases. However with Cleaner Production, Waste Minimization and Pollution Prevention concepts then Dnepr itself will very quickly be cleaned with the help of the sun, air, plants.

- This problem can be solved only systematically at various hierarchical levels, beginning not from person using drinking water, but from sources of its pollution - the industrial and agricultural enterprises, and municipal sources of pollution.

- 2. Region

Ukrainian (Kryviy Rig, Zhovti Vody and western Donbass) mine water refining for cleaner Black Sea

- Ukraine has a lot of mines every of which has sewage mine water (average flow in M3/H – 300 – 1000).
- This water contains high Ca, Sulphates, Chlorides, Heavy Metals salts etc, and needs to be subjected to system for the salt removal. It has no contaminations for biological treatment , therefore the system would be Ultra Filtration followed by Reverse Osmosis process.
Water will be thrown in hydrographic network Besides the part of water will be used for the equipment washing.

- Index of water quality and limits of concentration changes for the one of **Zhovti Vody** mine

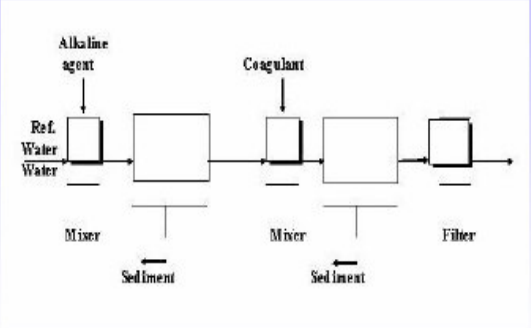
Composition of calcium (Ca^{+2}) -milligram/liter - 140,0-260,0
Iron (Fe all) -0,05
Ammonium (NH_4^+) -0,50-2,50
Chlorides (Cl^-)- 269,8-470,0
Sulphates (SO_4^{-2}) - 583,3-702,5
Nitrates (NO_3^-) - 10,0-140,0
Nitrites (NO_2^-) - 0,03-0,13
Phosphorus (P) - 0,2-0,33
Solid residual - 1553,0-1490,0
Oxygen demand - 10,0-30,0
Suspended matter - 26,2-10,0
Stickiness -Milligram- equivalent/ liter - 11,0-16,0
Reaction of environment (pH) - 8,0-8,5
Biological oxygen potential- 5 milligram/liter

- Unfortunately while Ukraine has no any solving, technology, equipment, power energy and money for mining water treatment.
- USA UEM Inc. proposed the general treatment scheme to meet the requirements of the mining production sewage treatment plants would be to treat approximately 70-75% of the effluent with a ultrafiltration system followed by a specialized reverse osmosis system with low fouling type membranes in the upper nanofilm category where the final permeate would be blended by with the remaining effluent. This blend would exceed the required concentration requirements and allow for adjustments in the flow and quality so as to be most efficient.

- Near Dnieper region is not only zone of metallurgy, chemistry, agriculture, but also zone of the advanced mechanical engineering. In view of it, it is possible to solve many regional water ecological problems, by basing on significant scientific and industrial potential of region.

- For the mining water treatment we can use our program of work on maintenance of the inhabitants of industrial city by qualitative drinking water including the use of new two step reagent technology of water preparation and its introduction without any reconstruction on acting water supplying plants, electrical pulsing and light disinfecting of water, creation of manufacture of local installations for disinfecting of water without chlorine processing.

- Increasing water pH to 11 will result in deposition of magnesium hydroxide and calcium carbonate under certain conditions in a mixing/precipitation tank. More than 90 % of the heavy metals and radionuclides, over 80 % of the organic contaminants and all bacterial pollutants are removed in the process. The final step is water neutralization with a hydrolysing coagulant (salt of aluminum or iron) for further purification. All additives are readily available. A mixing/ precipitation tank is the only necessary addition to the existing equipment.



- The present practice allows to carry out a complex clearing of water from heavy metals, (Fe, Mn, Al, Be, Cu, As, Pb, Zn, Se, Cd, Ti, Ni, Hg, Cr etc.); radioactive elements, (U, Th, Pb-210, Po-210, Sr-90, As-137, Ra-226); petroleum, pesticides, other organic inclusions with simultaneous water disinfecting without the application of chlorine and operating time of cancerogenous -organic derivatives. The level of water purification from this elements and combinations is from 92 to 98 percents, what is best in compare with traditional «chlorine» water purification technology in all municipal water treatment plants in the former Soviet Union.

- 3. City

- A lot of ways of the decision of a problem on this level of hierarchy are known in the world. Here is enough low- waste technologies, interbranch use of toxic waste on the base of industrial symbioses, local installations of clearing of emissions, etc. However, despite of rather fast offsetting, the work at the given level requires a lot of energy, rather large capital investments and in conditions of an economic crisis of Ukraine it is not necessary to expect fast realization of works on ecologization of pollution sources of water pool.

- It is possible and it is necessary to use as natural sources of energy for it (ultra-violet irradiation, oxygen of air, wind, and clearing with the help of plants (so-called, "FS-technology" of Zaporozhye scientists) etc. direction. However, and this direction requires large time and expenditures of labor for its realization.

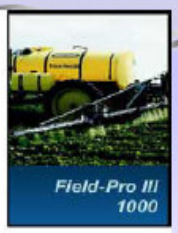
- Without contacts with a world ecological community, without investments of means of our businessmen and western investors in the decision of water ecological problems of Ukraine this process will be very long.
- To find means for creation of installations of clearing, we should use such modern market forms of work as leasing of water cleaning installations under guarantees of municipal soviets with return of the investments from additional means received from sale to the inhabitants of water with higher consumer properties.

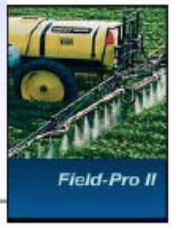
- Therefore we are in a searching of clearing water method with account of these circumstances. The purpose of the present researches is the development and introduction in a practice of the water preparing, shown earlier new technology (offered conjointly with B.Pismenny), based on application of practically the same reagents, that are applied in present time, without essential change of hardware registration process and exception of water chlorine processing.

- Hence, the specified technological decision does not require significant changes of a hardware part of the water preparing systems both requires only in additional sedimenter.
- As against existing technologies, an examined way allows to carry out a complex clearing of water from heavy metals, radioactive elements, petroleum, pesticides, other organic inclusions with simultaneous water disinfecting without the application of chlorine.

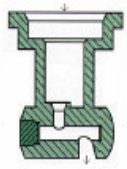
- 4. Enterprise

Electric aerosol spraying technology and equipment in Agriculture





- It is necessary to use high voltage to do ultra dispersion sawing and to charge the drops of active liquid to use this immediately to plants foliage treatment. This considerably brings down pesticide expense and liquidates contamination of earth by pesticides.

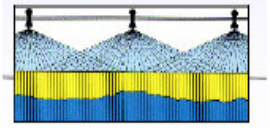


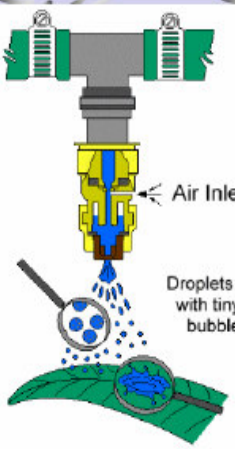
Electric aerosol spraying pulverizers, however, have a tendency to become blocked up when a liquid and/or air contain hard parts from dirt sand or dust. Furthermore, traditional pulverizers bulky and call for cables of high voltage. This makes them unsuitable for small plots of land, unreliable and expensive.

It is necessary to have more reliable, compact and safe and not such expensive pulverizers and methods of the sprinkling.

A Project aim is a development of aerosol spraying technology, which provides such improvement.

Materials, pulverizers construction and higher voltage are particularly importance, but main idea of our dispersion technology is organization of two-phasic (air – liquid) stream





- Our idea: Instead of liquid aerosol it is possible to use a liquid-gas mixture. Then sand, dust and dirt do not congest in pulverizer.
- A device of high voltage, that used, breaks down under automatic control block and converter of high voltage, that takes place by pulverizer for safety rise and underestimation of cost.

Safety:

- there are not cables of high voltage, high tension generates are in immediate nearness to pulverizer.
- foreseen spark blocking system with use of current stabilization and also turning off of device of high voltage, when a pulverizer comes around soil.
- Optimum action due to current stabilization.
- Compactness, small weight and reliable construction.
- It is possible autonomous power supplying.

- Development was approved in Ukraine. The consumption of pesticides was diminished into 2-5 times There are not observed aerosol losses on leaf when wind speed was to 5 m/s. It was marked that a foliage breaks out by aerosol from both sides, that added to pesticide action effect.
- Amount of treatments by aerosol can be minimized, that gives rise to underestimation actions on operators.

- The electric aerosol pulverizers with use of the compact electric accumulators for the first time were planned for small private gardens. They provide lowering from 5 to 6 once pesticide expenses. NIS is an enormous market for electric aerosol pulverizers. Only Ukraine has about 15,000,000 small private gardens, in that time, as western pulverizers are not adapted to our demands. China and other countries with small plots of land and dry regions with high dust maintenance in mid air, identical to East countries, Africa and North America, also can be by potential markets.

- In farming development can also use for sprinkling with pesticides, stimulators of growth or fertilizers and also for watering.
- Development also can be gone for ozonization and for workplace disinfection with use of anode water, for lead-in into medicines workplace, vitamins and other

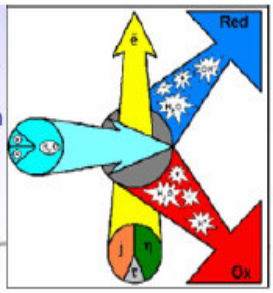
It Is possible to use the aerosol complexes with mechanical nebulizers for disinfecting in stock-raising, in medicine, on productions of food retail and pharmaceutical industry with anolit use

INSTALLATION FOR THE ACTIVATED WATER PRODUCTION

- The turbid whirlpool of legends and conjectures spins ROUND the activated (by an anode and cathode, "living" and "dead") water.
- Impermissible application of handicraft equipment and technologies. For electro-activators use proof materials: for making of cathodes is titan, anodes - platinum, specialcoverages, ultraclean graphite. For diaphragms apply the specialceramics or porous PTFE.

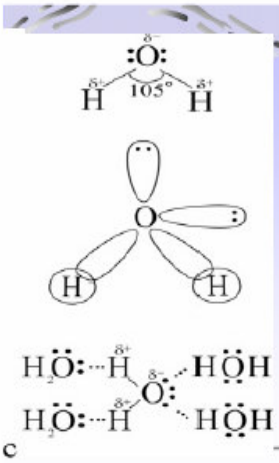
- The electro-activated water turns out admission of electric current through ordinary water or weak its solutions of salts by a concentration to 1%. The activated water possesses the wide spectrum of action due to large electric charges: to positive in acid water (anolite) and negative in alkaline water (catolite).

- The activated water finds wide application in a plant-grower for treatment of seed, in the poultry farming, stock-raising, for treatment of agricultural and fish product, production of food stuffs, for the use in medicine.

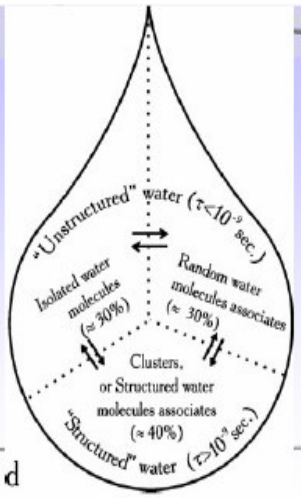


"Activator USUCE" is a device of continuous action of semistationary type, served one operator. The construction of electrolytic section eliminates a hit in water during its activating of heavy metals. An activator is supplied automation, disconnecting one from an electric network under reaching the consumable electric current of possible size - 40 A. Modulled continuous action electrolytic section includes: flow electrolytic cell; power module; control

- Every molecule of water is able to form four hydrogen connections: two – as a donor and two – as acceptor of proton. Thus for hydrogen and covalent connections, formed the atoms of oxygen, a certain mutual spatial orientation is characteristic. Due to hydrogen connections of molecule of water able to form not only casual acc, I.e. not having a well-organized structure but also clusters – associates, having a certain structure.



Between associates and clusters, and also into them there can be cavities, where separate molecules "roam" waters, unconnected hydrogen connections. These molecules constantly switch places with the molecules of H_2O, entering in associates and clusters. Mean time of life of molecule of water is in the linked state, I.e. in associates and clusters, $1x10^{-9}$ makes with.



Activated water application

- for watering of substratums at growing of vegetable plants with the purpose of stimulation of their growth and development, increases of the productivity to 15%;
- for wetting of seed with the purpose of increase of energy of germination and more intensive growth in a seedling period. Thus for one cultures cathode water is used, for other auxesis is anode water.

- CATHODE WATER is used also for adjustment of reaction of soil solution and solutions physiological sour mineral fertilizers, that allows to save their expense at the additional fertilizing to 20-25%.
- ANODE WATER can be used as ecologically clean method of fight against a plant louse, whitefly and hook-worm.

USING OF THE ELECTROCHEMICALLY ACTIVATED WATER FOR WASHING OF CONTAINER

- Using of the electrochemically activated water for washing of suckling container, cisterns, other tableware allows to eliminate the operations of mechanical delete of contaminations, decrease the expense of synthetic cleansers in 5-7 times, shorten twice time of treatment and simultaneously to promote quality of cleaning of surface of tableware from contaminations of all types. For washing alkalescent catholyte and weak-acid anolyte are used.

- "Dead" water (anolyte) has acid medium and renders a powerful disinfectant and sterilizing action. Therefore it can be used in the way of life - for disinfecting of drinking-water, treatment of apartments, wetting and bleaching of linen, treatment of tableware for preservation, fruit and root crops for the protracted treatment and making healthy of people and animals. Wide possibilities at anolyte and for clearing of muddy environments of waters. water conveyance systems, capacities for storage and portage of water, swimming pools and sources. Water of pool after addition of anolyte acquires light is turquoise, some smell and irritating operating on a skin and mucous membranes is absent.

- "Living" water (catholyte has an alkaline medium and is powerful biostimulant. Easily penetrates through biological membranes, stimulates the fermentative systems, activity of cages, processes of oxidation-reduction, prevents peroxide oxidization of lipids of cellular membranes (antioxidant), promotes mastering squeak, normalizes a cellular exchange, instrumental in destroying of slags and strengthens protective mechanisms.
- Used in medicine for treatment of wounds, ulcers. At the diseases of digestive highway, respiratory system, cardiovascular system, musculoskeletal systems, leather, urologies, gynaecological and many other diseases.

- Catholyte can be applied for strengthening of growth of plants, flowers, ; seedlings, they can desoxidate soil by watering or sprinkling.
- Treatment of forages, carrot, beet and other vegetables, fruit for the protracted storage (the term of storage is multiplied on 2 - 3 months). Apples, treated with Catholyte , save the freshness to May of next year. "K" - used for locks of seed, stimulations of growth of plants, strengthening of properties of the matters dissolved in him, "K" - not toxic and harmless.

INCREASE OF EFFICIENCY AND ECOLOGIZATION OF PLANT-GROWER AT COMPLEX ACTION OF THE ACTIVATED WATER

Cleaning and improvement of quality of underground chloridesodium and Fe-containing waters for an agricultural water-supply, including for irrigation;
Use of anolyte for the mordant of seed before sowing; long stratification of seed in anolyte and in solutions on this basis;
Application of Catholyte for presowing preparation of seed;

- Anolyte, catholyte and their mixture in course of time grow into ordinary water, besides fully or partly cleared. Anolyte saves the properties long time, the action of catholyte is limited, and mixture of Anolyte and catholyte is effective during a few clock. But early or late these "ingredients" are acquired by properties ecologically clean water, preliminary rendering the stimulant affecting seed or garden-stuffs (before sowing – landing) and on plants.

Aerosol generator of USUCE for the receipt of fog of anolyte:
The distinctive feature of new method of antimicrobial treatment is the use for this purpose of electric aerozol or electrochemically activated anolyte with the wide range of parameters on the nebulized solution.

Technical descriptions of generator of aerosol:

- diameter of aerosol cloud to 15 м humidity to 98%
- the productivity of 0,3 - 3 l/min. dispersion of aerosol of 5 - 50 мкм primary power supply 50 Hertzs 380 In (3 phases) maximal consumable power 2,5 kWt mass is general 15 kg
- of Research of efficiency of disinfecting of apartments a volume no less than 150 м3 by the aerosol of anolyte, showed that the assured level of decline of bacteria of Cereus semination spores is no less than two orders. Assured level of decline of semination by a vegetative form are seven orders.

Influence of the activated water on fattenings qualities of pigs

- The tendency of modern biotechnology is more wide application of natural biologically active additions of vegetable, animal and mineral origin. On the present numerous reports of domestic and foreign authors to biological stimulators can be taken water, passing the electrochemical activating.

- Animals, gettings the activated water, achieved for slaughter mass on 5-7 days before a control group.
- In experimental groups it was anymore than animals with maximal mass ("leaders").
- Additional weights in experimental groups were higher within the limits of 8-10% in relation to controls.
- Not a single case of case of animals is marked in experimental groups, while in a control group a case registered on the early terms of fattening up.
- The animals of experimental groups showed ordinary activity, well ate up a forage, had normal haematological indexes.
- Energies are expended on 1 kg of increase: by control - 7,21 к.ед; experimental - 5,63 - 6,09 к.ед.
- In the standards of meat and liver of animal experimental and controls groups it is not exposed reliable distinction in maintenance of protein and гликогена.
- Mass of the cut carcasses of animal experimental groups was higher controls on the average on 8-14 kg

5. House

- "House" – it may be a settlement, residential area, large house, school, children camping etc.). For this level it is possible to use one of two approaches: or to create stations of distribution of drinking water after its preliminary cleaning (it is possible to address to experience of Turkey, Germany and another countries), or to apply modular installations of water clearing of domestic and western manufacture to a house, settlement, camp etc.

- 6. Flat
- 7. Inhabitant

- And, at last, this level is an urban apartment, where is possible as cleaning only of drinking water in flowing and periodic clearing devices, and also cleaning of all water submitted in an apartment (in basic, local installations). The work with this level is most expensive, socially oriented only on the persons with a rather high level of the incomes.

- There are a lot of types of the domestic and import filters, free selling in the market under the characteristics frequently do not correspond to the requirements of operation and structure of cleared water.In a trade network there are approximately 50 types of domestic and foreign designs of filters of cost from 10 up to 2500 USD. They differ not only with price, but also productivity, principle of action, expense of energy, duration of work and throughput, efficiency of clearing and kind of removal components. How to choose suitable filter, how to be guided in this sea of designs with the account not always of diligent advertising, according to which each filter is the best, most reliable, etc...

- To take even available in a lot of Ukrainian shops, water cleaners with a bubbles flotation "AQUALEGY", developed in Dnepropetrovsk. Three enterprises already have manufactures of such installations. Whether it is necessary to inhabitants, or it is better to use money more reasonably? The opinions of the experts here were divided. The installation authors insist that "AQUALEGY" is the new word in water cleaning engineering and this cleaner is the best of all another, as its efficiency is confirmed by the appropriate certificate of the Kiev experts.

- But testing in Kiev scientific - hygienic center was carried out in suburb, where air is much cleaner, than it is in city, and not in kitchen with a gas cooker, but in analytical laboratory. And in industrial city, for sample. Dnepropetrovsk, there is a lot of sources of pollution of air, which in general are not present in suburb of Kiev.
- And, at last, many micro-organisms available in air, including dangerous, can remain in water with its "clearing" air and to be made quickly multiple copies in environment, enriched with oxygen.

- Here rather problematic clearing of water of all this "bouquet" with the help bubbles flotation cleaners without preliminary clearing of air submitted on clearing of water, and also owing to uncontrollable and astable quantity of soap in initial water also is represented to a number of the experts. Who is right in this discussion concerning of human health ?
- As to widely promoted filters "Britta", their consumer qualities are not corresponded to price. Users have paid attention that the spare filtering element for filters of this type, which defines all parameters of the filter, has price about 5 USD., but plastic box, where it is inserted, - 40-45 USD. May be it is too expensive box?

- Unfortunately, nobody coordinates the research works on creation of designs of individual household cleaner of drinking water, the examinations are not be carried out. What to buy today? In opinion of our experts the cheapest membrane filters " Crimean dew " and Kiev filters "Crystal" are the most corresponded to the conditions of Ukrainian industrial cities.
- And nevertheless even the best filters and cleaners do not solve completely problem of maintenance of population qualitative water.

- This problem can be solved only systematically at various hierarchical levels, beginning not from person using drinking water, but from sources of its pollution - the industrial and agricultural enterprises, and municipal sources of pollution.

Thank you for your attention!

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TREATMENT OF THE RESIDUAL FRACTION OF DOMESTIC WASTE: THE FLEMISH CASE

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Abstract

Grate furnace incineration is the most commonly used technology for thermal treatment of the (residual fraction of) domestic and comparable industrial waste. Although it is a proven technology, it is continuously being improved and research is carried out in order to make it more sustainable. Such developments are mainly relative to flue gas treatment, energy recovery, ash treatment in view of recycling, zero wastewater discharge, etc. A state-of-the-art integrated installation where many such developments were and are being realised is described along with current research on bottom ash recycling.

Mechanical-biological treatment techniques are more and more used as alternative to landfilling and incineration of the (residual fraction of) domestic and comparable industrial waste. Some relevant techniques of different types (biological drying and separation, separation and biological digestion, steam digestion and separation) are described and discussed. The technologies considered are then evaluated and compared.

Some attention will also be given to fluid bed incineration, which is an upcoming alternative and offers high potential for treatment of the refuse derived fuel from mechanical biological treatment along with high calorific waste from industrial origin, sludge from municipal wastewater treatment and mixed municipal waste.

Cleaner Production in Integrated Treatment of Domestic and comparable Industrial Waste using a Grate Furnace

Carlo Vandecasteele, K.U.Leuven, Belgium
Guido Wauters, Indaver, Belgium

Introduction

Authorities in Flanders stimulate since 15 years the following hierarchy for domestic waste treatment:

- Prevention
- Maximisation of recycling
- Incineration of residual fraction with energy recovery

This target is realised by :

- Organisation of collection by local municipal authorities
- Selective collection of recyclable fractions
- Ban on landfilling of recyclable and combustible waste or waste fractions
- Taxes on landfilling (5-10 times higher) and incineration

Introduction

Assumed that selective collection of recyclable fraction at the source best guarantee of high quality recycling

2003: 3.2 miljon ton of domestic waste/year were produced (535 kg/inhabitant)

70% collected selectively

30% residual waste:25 % incinerated
5% landfilled

Introduction

- Selectively collected:
  - Composted: 35.6%
  - Reused: 4.0%
  - Recycled: 57.8%
  - Landfilled or incinerated: 2.6%
- Not selectively collected: 161 kg/inhabitant
  - Subject of this presentation
  - Treated in same installations as comparable industrial waste and residues from treatment of selectively collected fractions and waste water treatment sludge: **'domestic and comparable industrial waste'**

Introduction

- Incineration: proven, safe, economic
  - State -of -the -art integrated grate-furnace incineration plant
  - Recent developments

Integrated solid waste treatment using grate furnace incinerator technology

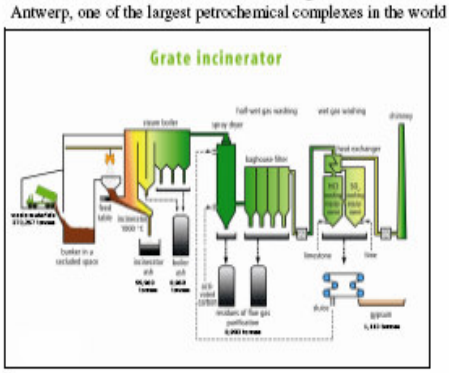
- Indaver is the most important waste treatment company in Flanders (1.8 10^6 /year in 2004)
- Grate furnace complex of Indaver in Beveren (Antwerp): 400 10^3 ton of domestic waste in 2004
- 3 grate furnace lines
- Nominal capacity: 48.1 ton/h

Cleaner production aspects

In the integrated facility (grate furnace incinerators, bottom ash treatment) around these grate furnace incinerators, Indaver addressed all relevant aspects of cleaner production:

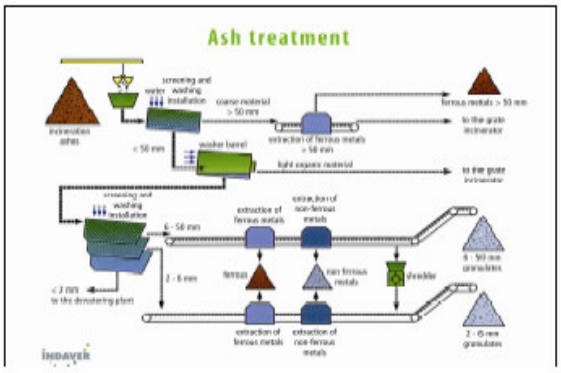
- recycling of energy
- recycling of waste and by-products (bottom ash);
- minimal emissions to air, water and soil.
- minimal use of resources and auxiliaries (water)

Indaver incineration plant situated in Antwerp, one of the largest petrochemical complexes in the world



Wet bottom ash treatment

capacity: 165 kton/year; aged to decrease leaching



Energy recovery

- Energy recovery
  - 150 ton/h of steam (400°C, 40 bar)
    - Used in installation
    - To energy supplier > industrial companies
    - Turbine driven generator > network
  - Energy made available through 2 carriers: steam and electricity
  - Gross energy conv. yield: 50.2 %, net: 40.8%

Material recovery

Fraction	Application	Weight% of bottomash	Weight% of waste
Ferrous metal	Recycling, highest quality	8.5	2.5 -3
Non ferrous metal	Recycling, highest quality	1	
Granulate 2-6 mm	Granular or monolithic application in constructions	14	10-12
Granulate 6-50 mm	Granular applications in constructions	27	
Total of applications without further monitoring		50.5	13.5
Sand 0.1-2 mm	Controlled application in constructions or landfill	32	8.6
Total of applications with further monitoring		32	8.6
Sludge <0.1 mm	Landfill	8	
Organic	Returned to grate furnace	1	
Other	Landfill	8.5	
Total to be disposed of		17.5	4.7

Material recovery

Parameter	Fraction		VLAREA limit value
	2-6 mm	6-50 mm	
Dioxins	<5 pg TEQ/g	<5 pg TEQ/g	
PAH (individual values)	<0.03 mg/kg DM	<0.03 mg/kg DM	
Metal leaching (mg/kg)			
As	<0.025	<0.05	0.8
Cd	<0.01	<0.01	0.03
Cr	<0.03	<0.05	0.5
Cu	0.17-0.50	0.04-0.40	0.5
Pb	<0.03	<0.10	1.3
Ni	<0.025	<0.05	0.75
Zn	<0.03	<0.10	2.8

Concentration of dioxins and PAHs and metal leaching data for granulates after 3 months of ageing

- Dioxins and PAH very low
- Only Cu leaching is critical
- Certificates for use as secondary raw material for granulates, not for sand: Cu leaching too high

Flue gas treatment

Parameter	Emission concentration (mg/Nm³)			Emission (ton/year)	
	2000	2004	limit value	2000	2004
HCl	29.5	0.8	10	34.0	2.15
SO_2	40.0	2.1	50	48.6	5.6

- In 2001 wet scrubbing added. HCl and SO_2 well below limit
- Other emission concentrations below limit values
- Annual dioxin emission 0.05 g TEQ negligible to 80 g TEQ for Flanders (2003)

Water consumption and waste water discharge

- Main water consuming parts: boiler, spray dryer, wet scrubbing, ash treatment
- Fresh and contaminated water, 30% rain water
- Ash treatment: contaminated rain water (from storage tank), recycled
- Wet scrubbing: non-contaminated rain water (roofs)
- All water (wet scrubbing, …) evaporated in spraydrier
- Impurities retained on fabric filters
- Zero water discharge

Research on bottom ash treatment

- Cu leaching from sand (0.1-2 mm) fraction exceeds Vlarea limit value (0.5 mg/kg dry matter)
- Research on additional treatment:
  - heating,
  - extraction,
  - accelerated carbonation

Research on bottom ash treatment

- Heating
  - 1-2 % organic carbon, responsible for enhanced Cu leaching
  - Heating volatilises or decomposes organic matter
  - Fulvic acid responsible?

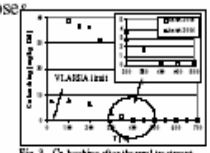
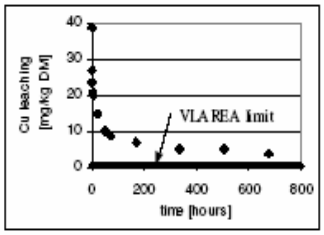


Fig. 3- Cu leaching after thermal treatment of sand fraction (50g, 2 hours).

•Accelerated carbonation: 10% CO2, 50°C

•Why? pH and carbonate formation do not explain influence of CO2



Research on bottom ash treatment

- Extraction : 1M ammoniumcitrate, L/S=5, 1h, followed by 3 washing steps (L/S=5, 1h)

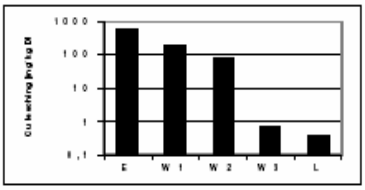


Fig. 4 - Cu release (sand fraction) during extraction process.

TREATMENT OF WASTEWATERS THROUGH ADSORPTION OF HEAVY METALS BY NATURAL CLAY

K.T.Ewida[1], **D.S.Elmonayeri** [2], **M.R.Ezz El. Din** [3], **M.S. Ghaly** [4]

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Abstract

In Egypt, the increase in industrial activities over the past years has contributed significantly to the deterioration of environmental conditions in urban conglomerates and localities nationwide. As anticipated, this industrial activity increase was accompanied by an increase in ambient pollutant levels and generation of large amounts of hazardous wastes. With the lack of a system to regulate the handling or disposal of the generated wastes, each industrial facility was left unchallenged to devise its own waste management procedures. Recently, many naturally occurring materials have been used for different decontamination purposes. The natural clay minerals are considered as a good ion exchanger, since it is easily found and have low cost and high capacity in removing the heavy metals and organic compounds.

The objective of this work is to study the sorption behavior of some heavy metals present in the industrial waste solutions using some clay mineral materials collected from different locations in Egypt.

In this concern, five clay samples collected from Sinai, El-Safe, El-Fayoum, Bahryia and Aswan were used for this study.

The adsorption studies were carried out in two stages. In the first stage a batch process equilibrium was carried out for single component using synthetic solutions with initial concentrations in the range between 2.5 to 10 mg/l of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2}. The adsorption capacities of the collected clay samples were as follows: -

For clay sample collected from Sinai the adsorption capacity was 9.6, 21.6, 8.4 and 6.2 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively. For El- Fayoum clay sample the adsorption capacity, was 16.8, 27.6, 15.0 and 17.0 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively. For Bahryia clay sample the adsorption capacity, was 12.0, 22.5, 9.0 and 9.6 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively.

Finally for the Aswan sample the adsorption capacity was 13.0, 26.1, 11.6 and 10.0 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively.

The best adsorption capacity was found for El- Fayoum clay sample while the lowest on was found for clay sample collected from Sinai site. The adsorption isotherms of Langmiur and Freundlish were also tested and it is found that El- Fayoum clay sample has the highest adsorption capacity. The results have been proven the favourability of such adsorbents for the removal of lead, iron, copper and zinc salts from their waste solutions. The parameters (n) of Freundlish was found to be more than one and separation factor (R) of Langmiur was found to be between zero and one.

The second stage of the work was carried out using fixed bed column. El-Fayoum clay sample was used for treating the synthetic waste solutions containing 10 ppm of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. And after the treatment it was found that more than 90% of the investigated elements were removed. We can conclude from the above results that the natural clay collected from El-Fayoum site can be considered as an efficient sorbent for metal cations from their aqueous solution and can be used for the treatment of the industrial waste solutions. In addition, it is abundant, easily found and have low cost of processing.

Treatment of wastewaters through adsorption of heavy metals by natural clay

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1

Abstract

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2

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- The adsorption study was carried out in stage, and a batch process equilibrium was carried out for single component using synthetic solutions with initial concentrations in the range between 2.5 to 10 mg/l of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2}. The adsorption capacities of the collected clay samples were as follows: -
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3

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4

Introduction:

- Natural clay minerals have recently become of great importance as an absorption media for the removal of several pollutants from polluted waters. This is due to the fact that they are good ion exchangers, easily found, and their high capacity in removing heavy metals and organic compounds. Stevenson,(1), Taylor (2).
- Clay minerals can be grouped into four main categories:

Montmorillonite, Kaolinite, illites, and vermiculite. Some distinguished characteristics of these common clay types are given in table (1)

5

Table (1): Cation Exchange Capacities and Specific Surface Areas of four common Clay Minerals*.

Clay Type	Specific Surface Area (m^2/g)	Cation Exchange Capacity (meq/100g)
Vermicuite	600-800	100-150
Montmorillonite	600-800	80-150
Illite	65-100	10-100
Kaolinite	7-30	3-15

*(Stevenson, 1982)

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Treatment of wastewaters through adsorption of heavy metals by natural clay

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1

Abstract

In Egypt, the increase in industrial activities over the past years has contributed significantly to the deterioration of environmental conditions in urban conglomerates and localities nationwide. As anticipated, this increase in industrial activity was accompanied by an increase in ambient pollutant levels and generation of large amounts of hazardous wastes. With the lack of a system to regulate the handling or disposal of the generated wastes, each industrial facility was left unchallenged to devise its own waste management procedures. Recently, many naturally occurring materials have been used for different decontamination purposes. The natural clay minerals are considered as a good ion exchanger, since it is easily found and have low cost and high capacity in removing the heavy metals and organic compounds.

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- The objective of this work is to study the sorption behavior of some heavy metals present in the industrial waste solutions using some clay mineral materials collected from different locations in Egypt.
- In this concern, five clay samples collected from Sinai, El-Safe, El-Fayoum, Bahryia and Aswan were used for this study.
- The adsorption study was carried out in stage, and a batch process equilibrium was carried out for single component using synthetic solutions with initial concentrations in the range between 2.5 to 10 mg/l of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2}. The adsorption capacities of the collected clay samples were as follows: -
- For clay sample collected from Sinai the adsorption capacity was 9.6, 21.6, 8.4 and 6.2 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively. For El- Fayoum clay sample the adsorption capacity, was 16.8, 27.6, 15.0 and 17.0 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively. For Bahryia clay sample the adsorption capacity, was 12.0, 22.5, 9.0 and 9.6 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively.

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Finally for the Aswan sample the adsorption capacity was 13.0, 26.1, 11.6 and 10.0 mg/g of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} respectively.

The best adsorption capacity was found for El- Fayoum clay sample while the lowest on was found for clay sample collected from Sinai site. The adsorption isotherms of Langmiur and Freundlish were also tested and it is found that El- Fayoum clay sample has the highest adsorption capacity. The results have proven the favourablity of such adsorbents for the removal of lead, iron, copper and zinc salts from their waste solutions. The parameters (v) of Freundlish was found to be more than one and separation factor (R) of Langmiur was found to be between zero and one.

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Introduction:

- Natural clay minerals have recently become of great importance as an absorption media for the removal of several pollutants from polluted waters. This is due to the fact that they are good ion exchangers, easily found, and their high capacity in removing heavy metals and organic compounds. Stevenson,(1), Taylor (2).
- Clay minerals can be grouped into four main categories:

Montmorillonite, Kaolinite, illites, and vermiculite. Some distinguished characteristics of these common clay types are given in table (1)

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Table (1): Cation Exchange Capacities and Specific Surface Areas of four common Clay Minerals*.

Clay Type	Specific Surface Area (m^2/g)	Cation Exchange Capacity (meq/100g)
Vermicuite	600-800	100-150
Montmorillonite	600-800	80-150
Illite	65-100	10-100
Kaolinite	7-30	3-15

*(Stevenson, 1982)

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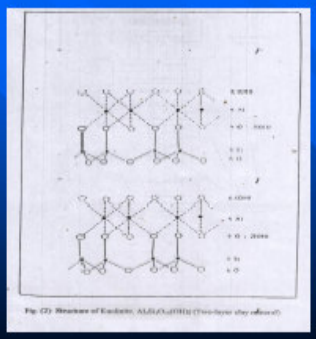
Fig. (2): Structure of Kaolinite, $Al_4Si_4O_{10}(OH)_8$ (Two-layer clay mineral) (**Stevenson, 1982**).



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- The source of negative charges on the broken edges of kaolinite, as well as other clays, is believed to arise from dissociation of a proton (H^+) from an exposed OH group. This is possible because oxygen atoms at the edges are in contract with one rather than two Si or Al atoms. The hydrogens of tetrahedral OH·s (those associated with Al). See fig. (3). As one might expect, dissociation is strongly pH dependent.

- Discrete positive site are also possible at edges, particulary at low pH·s, through protonation of OH groups forming (OH_2^+).

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Fig. (3): Distribution of Charge and Cation Exchange Potential of Clay (**Stevenson, 1982**).

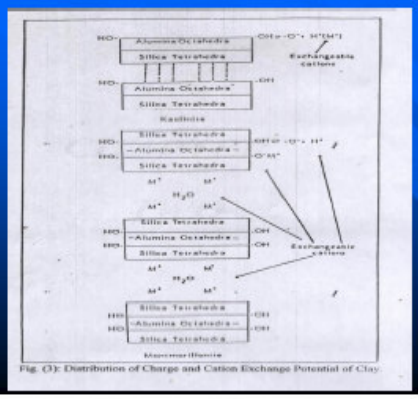

Fig. (3): Distribution of Charge and Cation Exchange Potential of Clay

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•In the natural state the surfaces of clay minerals are hydrated. This surface water is believed to be less dense (more ordered) than water and said to have an "icelike" syructure. A dsorbed ions are to some extent associated with water molecules at the surface and are themselves hydrated. Hydration and coordinated water molecules are believed to play an important role in adsorption reactions (**Stevenson, 1982**).

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Adsorption of heavy metals by natural clay

(**John et al., 1975**) discussed the possibility of removing iron and manganese from waste water using zeolite and vermiculite clay . The adsorption on Zeolite took place where iron and manganese concentrations have a low values, less than 0.5mg/L because accumulations of precipitates of these metals . These effects may cause the exchange medium to lose its capacity, But in case of using vermiculite clay, a high concentration can be removed in least time. The vermiculite clay has a high capacity for removing of most heavy metal and also when vermiculite treated with solutions of Mn^{++} and MnO_4 become coated with MnO_2. This coating is then capable of sorbing of Fe(II) and Mn(II). Also, (**Willey and Jenning, 1963**) used zeoite clay for the removing of iron and manganese from wastewater. The zeoite capacity for either iron or manganese removal is 1.46 mg/g.

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(**Das et. al., 1991**) studied the metal adsorption properties of vermiculite through removing of lead from water solution. The batch sorption kinetics can be described by a first order reversible reaction and the equilibrium follow the Frendlich adsorption isotherm. The up take of lead is a function of the pH of the medium and is maximal at pH=6. On the other hand, (**Kugler, et. al. 2002**) showed the potential of modified montmorillonite clays as low-cost adsorbents/ion-exchangers for the removal of trace level heavy metals (Cd, Cu, Ni, Pb and Zn) from potable water and showed that all of the clays are selective for Pb and Cu adsorption from aqueous solutions at the mildly acidic pH range in which the the experiments were performed (pH 5.5-6). Also (**Saha, et. al. 2002**) examined the adsorption behavior of Cd, Zn and Pb from mixed solutions while (**Papini, et. al., 2002**) studied the removal of Lead onto Red soil .

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These soils are becoming interesting because of their large of availability in central and southern Italy and large attenuation capacity (21.7 mg/g for lead) with respect to heavy metals due to their geochemical characteristics (high surface area , cation-exchange capacity, and pH). Lead adsorption has been studied as a function of different pHs (4-7) were used in order to obtain different lead speciation in the liquid phase.

(**Tarasevich and Klimova, 2001**) developed the sorbents for the adsorption of heavy metal ions from water solutions by the modification of kaolinite, meta-kaolinite and aluminium oxyhydride by polyphosphates. The adsorption isotherms of Ni^{2+}, Co^{2+} and Cr^{3+} at the adsorbents prepared in this way demonstrated high adsorption capacity (300 to 100 mg/g depending on the sorbent type) and high selectivity of the materials with respect to the sorbed cations. The decrease of pH to 2 results in the almost complete desorption of heavy metal ions from the adsobent surface.

3

The investigations by (**Taylor, et al., 2000**) In this study, Ferich smectite, montmorillonite, illite, vermiculite and kaolinite were carried out to determine reactivity in sorption- reduction of Cr(VI) and it was found that the pH of the aqueous system affected both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqeous and adsorbed species.

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(**Loretta and Raymond, 2000**) studied the effect of H^+ ions on the adsorption and removal of Pb^{2+}ions from contaminated soil using kaolinite and illitic soils with pH 3.9 and 9.2. The adsorption-desorption characteristics of Pb^{2+} ions were determined using batch equilibrium tests and acid leach tests with various acids used to leach the soils. Under the same adsorption conditions, illitic soil adsorbed much more pb super 2 super plus ions than kaolinite. Also, (**Jain and Ali, 2000**) investigated the effect of solution pH, sediment does, contact time, and particle size on the adsorption of cadmium ions on bed sediments for a highly polluted river in western Uttar Pradesh, India. The role of the coarser sediment and the clay and silt fraction has been examined .The Langmuir and Freundlich adsorption models were used to determine the mechanistic parameters associated with the adsorption process.

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(**Garcia, et. al., 1999**) studied the sorption by different silicate minerals of some heavy metals, present in industrial waste water by low-cost mineral silicates. These adsorbents (mainly clay minerals) are ready available, the results show that some mineral species are suitable for the purification of such residual waters down to the limits prescribed by current legislation concerning industrial wastes. The Langmuir model was found to describe such adsorption processes best. The capacities depending on the metal adsorbed in the order: $Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. This mineral shows the highest sorption capacity relative to the other minerals studied. Factors in the reaction medium such as pH and ionic strength influenced the adsorption process. Also, (**Atanassova, 1999**) evaluated the effect of competing Cu, Zn, Cd and Ni ions in ,01 M Ca(NO sub 3) sub 2 on heavy metal sorption and desorption by soil clay fractions. Total sorption of Zn and Cd generally decreased in the order: Vertisol greater than Gleyic Acrisol greater than Planosol clay. At the conditions studied, Ni and Cd remain a ready source of pollution hazard. On the other hand, (**Tsai and Vesilined, 1999**) investigated the adsorption mechanisms of Zn(II) on lime-treated montmorillonite clay. At low Zn(II) concentrations, chemisorption affected the amount of Zn(II) adsorbed by montmorillonite. At high Zn(II) concentrations, physisorption was the dominant mechanism for Zn(II) adsorption. Lime enhanced the ability of montmorillonite to adsorb Zn(II) at low initial Zn(II) concentrations, but did not affect the ability of montmorillonite of adsorb Zn(II) at high initial Zn(II) concentrations.

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the investigation by (**Rauf, et al., 1999**) showed that the ability of bentonite to remove Cu from aqueous and acidic solutions at different pH values by varing the amount of adsorbent, temperature and shaking time. The maximum adsorption of Cu was achieved from aqueous solution at pH 3.8 and could be described by both the Langmuir and the Freundlich isotherms. But, (**Malakul et. al., 1998**) designed Several modified clays and created for selective removal and recovery of heavy metals such as Cd, Cu, Cr, etc. The metal adsorption has been shown to be mainly through chemical complexation rather than ion exchange. The immobilization of the metal ions is pH dependent. Also, (**Suraj, et. al., 1998**) studied adsorption of cadmium and copper on these modified kaolinites as a function of equilibrium time and temperature. The uptake of Cd and Cu at 30, 40, 50 and 60 degree C displayed similar kinetics with maximum uptake at 40 degree C for Cd and Cu. And (**Chen, et. al., 1998**) studied the interaction of $FeCl_3$ with sodium montmorillonite in dilute aqueous suspension.

7

EXPERIMENTAL

1

The experimental study in this research was to establish the optimum conditions for the removal of some heavy metals (Lead, Iron, Copper and Zinc) from their waste solutions. In this respect an exploratory investigation was carried out using the clay minerals to test the feasibility of using them for decontamination purposes and volume reduction.

2

Bi- distilled water was used for dissolution and dilution of chemicals as well as for washing all glasses. Samples and chemicals were weighted using an analytical balance which has a maximum sensitivity up to 0.1 mg. The other used equipment will be described below in the appreciated situations.

3

The adsorbates used in the study are five different clay samples collected from different locations in Egypt. These locations are at Sinai, El-Fayoum, El-Saff, Bahryia oasis, and at Aswan. From each location two samples were collected, grounded and mixed. The quartering technique was used to get a representative sample **(Jackson 1956),**

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- The Lead, Iron, and Zinc were used as salts in the chloride forms. In addition to copper sulphate was also used.

5

Mineralogical Analysis of the clay samples

Data on the mineralogical analysis are presented in table (6). These data show that, the clay samples collected from the different locations consist of kaolinate, quartz, and trace of montmorillonite. On the other hand, interstratified and montmorillonite are the most abundant mineral present in sample collected from El-Fayoum site.

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Chemical Composition of clay samples

The clay samples were chemically analyzed in order to determine the major and trace elements present in this samples. The data of the chemical analysis for the different clay samples are present in table (7). The main component is silica which is inactive materials but also it contains large percentage of active materials such as AL_2O_3, Fe_2O_3, MgO and CaO.

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Table (6): Mineralogical Analysis of clay Samples*.

Location / Mineral	Aswan	Sinai	EL-Saff	Bahryia	El-Fayoum
Kaolinite	Dom	Dom	Few	Trace	Few
Illite	Trace	–	Trace	Dom	Trace
Montmorillonite	trace	trace	Mode	Trace	Dom
Quartz	trace	Com	Few	Few	trace
Dolomite	Few	–	–	--	–
Interstratified	trace	–	Dom	Few	Com
Felspars	–	Few	Trace	Trace	Trace
Vermiculite	Few		Few	--	–

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Dom=Dominant >40%

Com=Common 25-40%

Few = Few 5-15%

Mod=Moderate 15-25%

Tra= Trace <5%

9

Table (7): Chemical Analysis of Clay Samples*.

Sample / Oxides	Aswan	Sinai	El-Saff	Bahryia	El-Fayoum
SiO_2	55.40	65.90	41.40	51.35	48.21
Al_2O_3	24.30	18.20	38.20	11.31	19.44
Fe_2O_3	8.58	0.64	5.72	18.02	3.10
MnO	0.74	0.05	0.49	3.39	0.03
MgO	2.42	1.12	–	0.35	–
CaO	0.58	0.25	0.76	3.26	3.98
Na_2O	0.19	0.05	1.41	0.23	2.30
K_2O	–	--	0.65	–	0.15
P_2O_5	1.29	1.37	–	1.10	–
TiO_2	1.08	0.007	2.20	0.03	1.40
CuO	0.01	0.002	0.30	0.02	–
L.O.I (mainly CO2)	6.5	12.39	8.78	10.92	12.19
Total	101.09	100.229	99.2	99.72	99.8

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Sorption of heavy metals by the investigated natural materials

- Batch equilibrium is the most common technique used for measuring sorption of heavy metal ion by natural material . All selected samples were conducted in batch technique at room temperature (26 ±1C°), in order to study the distribution of the selected heavy metal ion between the investigated material and liquid phase after set of reaction time.
- Preliminary experiments showed that the clay sample of weight of 0.05 g was found to be suitable for a solution of volume 50 ml to obtain a reasonable measurable distribution (Kd) with an error not more than ± 1.1 % The temperature, during the experiments, was about 26 ± 1 oC,
- $Kd = [(C_0-C_e)/C_e] . V/m$ (ml/g) (3-1)

11

- ***Where:***

- Co is the initial concentration in the aqueous phase (mg/l).

- Ce is the final concentration in the aqueous phase at equilibrium (mg/l).

- V is the volume of the aqueous phase (ml).

- m is the weight of the clay sample (g).

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• In all experiments, the solution that contained the heavy metal was mixed well using shaker with the clay samples until equilibrium was attained. The obtained data were presented in the form of uptake percent (U %) using the following formula:

$$U\,\% = [\,(C_0 - C_e)/C_0\,] \,.\, 100 \qquad (3\text{-}2)$$

13

Experimental Techniques for Batch Sorption Studies

- The required amount of each clay sample (m = 0.05 g) was weighed (in dry condition) into 100 ml dry polyethylene bottle. Then 50 ml of the respective heavy metal solution was added to each bottle. The bottles were closed with polyethylene stopper and shaken at room temperature using mechanical shaker with adjustable speed 700 oscillations per minute. After desired time of shaking each bottle was centrifuged at 3000 rpm for 10 minutes fig (6) and 3 ml of clear supernatant was pipetted into glass vial to measure the metal ion concentration using **Atomic Adsorption instrument**

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Factors affecting sorption process

The sorption of the investigated heavy metal on the select clay samples was found to be affected by the following factors :

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a- Contact time

To study the effect of changing the contact time on sorption of heavy metal ions by the clay samples was studied. It was performed using the abovementioned procedures. Different bottle samples were used and each bottle represents certain interval times [5, 10, 15, 20, 30, 60, 120] min.

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b- Hydrogen ion concentration (PH)

- The effect of changing the pH of the solution on the sorption of the investigated heavy metals by the clay samples was studied. The previously mentioned technique was applied. The pH was adjusted to the required values by adding dilute solution of HCl and/or NaOH, and measured.

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c- Equilibrium isotherm experiments

- Equilibrium isotherms were determined by the bottle- point method **(El-Dib and Badaway, 1979).** A fixed amount (0.05g) of adsorbent was added to bottles containing 0.05 L of metal solution at different initial concentrations C_0 (2.5ppm, 5ppm, 7.5ppm, 10ppm and 20ppm). The bottles were sealed and shaked at room temperature. till equilibrium is attained. Resultant solution concentration (C_e) was determined by Atomic Adsorption instrument. The difference between the initial metal concentration C_o and the equilibrium concentration C_e was used to compute the amount of metal removed (q_e) from the solution as follows:
- $q_e = [V\,(C_0 - C_e)]/m$ (mg/g)……..……..(3-3)

18

d- Competing ion concentration

- In studying the effect of competing cations on sorption of the investigated heavy metal ions Pb^{2+},Fe^{3+},Cu^{2+} and Zn^{2+}, two cations (Ca^{2+} and Mg^{2+}) were chosen to elucidate this competition. that probably exist in wastewater were chosen; Ca^{2+} was chosen as a competing cation for Pb^{2+} and Mg^{2+} were chosen as a competing cation for Fe^{3+}, Cu^{2+} and Zn^{2+}. The above mentioned technique was also applied.

19

e- Desorption study

- Desorption or release experiments were carried out on the loaded clay resulting from the equilibrium sorption experiments. The desorption process was studied taking in consideration the effect of the remaining unadsorbed solution remaining incorporated within the clay sample. This solution can not be completely withdrawn where 1 ml of clear supernatant was left in the bottle together with the solid phase. The 49 ml of desorbed solutions water, 0.1N HCl and $Ca^{2+}(No_3)$ were added and the closed polyethylene bottles were shaken for the desired time. Finally, the bottle was centrifuged for 10 min and 3 ml of the supernatant was withdrawn for measurements. Desorption (D) was evaluated using the following formula:
- $D\% = [(C_d - xC_t)/(C_0 - C_t)]. 100$ (3-4)

20

Where:

C_d is the concentration of the respective metal ion desorption solution,

x is the volume fraction of solution left initially with the clay sample.

C_t is the concentration at certain time.

21

RESULTS AND DISCUSSION

1

Sorption of heavy metals by Different clay Samples

- In the study of the sorption of different heavy metals using different types of clay samples, the different parameters affecting the sorption process were investigated. These parameters include contact time, the pH, adsorption equilibrium and the presence of competing ions.
- Batch equilibrium is the most commonly used technique for measuring heavy metals sorption on clay. It consists basically of contacting spiked solution with a clay samples and measuring the distribution of the investigated element between the clay and liquid phase after a set contact time. The sorption of the heavy metal ion is expressed by the percent uptake (%Uptake).

2

Effect of Contact Time on Sorption of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} by The Different Clay Samples.

- To study the capacity of the investigated clay samples to adsorb the heavy metals, experiments were carried out on the five chosen samples using solutions of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. The variation of percent uptake of the ion as a function of contact time is presented in figs. (7-10). From these figures it is clear that the sorption of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} increases with time to reach a saturation level depending on the type of the element, nature of the clay sample and to some extent to chemical composition of the aqueous phase. Figure (7) shows the variation of percent uptake of Pb^{2+} as a function of time for the five selected samples. From this fig., it was clear that the studied clay samples show relatively high affinity towards Pb^{2+} and the maximum uptake was attained after 20 min. and reach about 84% for the sample collected from El-Fayoum , 82% for El- Saff clay sample, 65% for Aswan clay sample and 60%for Bahryia clay sample .

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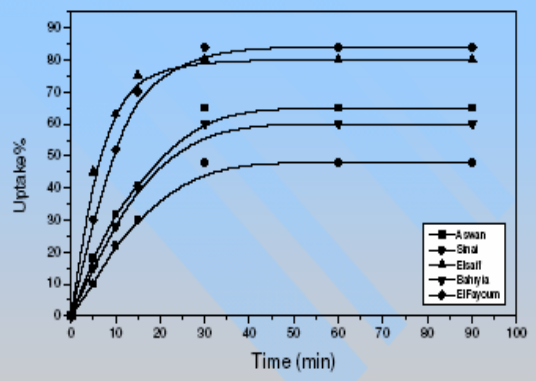

Fig. (7) Effect of contact time on sorption of Pb^{2+} by different clay samples.

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On the other hand, the sample collected from Sinai show a relative low adsorption capacity (48% uptake) to sorb Pb^{2+} ion and the maximum uptake was attained after 40 min. The capacity of each sample is varied from one to another and follows the order:

El-Fayoum >El-saff > Aswan > Bahryia > Sinai.

This may be attributed to the mineralogical and chemical composition of each sample. In fact, Pb^{2+} is easily incorporate into the crystal lattice of kaolinite and montorillonite mineral or to make ionic exchange with Na^{+} or K^{+} ions. **(Jain and Ram, 1997).**

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Figure (8) shows the variation of percent uptake of Fe^{3+} as a function of contact time. From this figure it is clear that clay sample collected from El-fayoum site has the highest sorption capacity towards Fe^{3+} followed by El- saff sample and Aswan samples. The sample collected from Sinai site has the lowest capacity while samples collected from Bahryia showed a moderate capacity towards Fe^{3+}. These observations may be due to the exchange of Fe^{3+} with Al^{3+} exiting in the aluminum silicate minerals **(Willey and Jenning ; 1963).**

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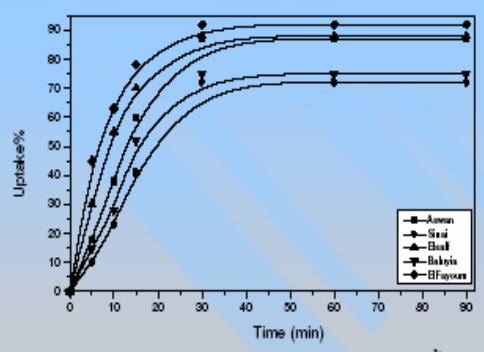

Fig.(8):Effect of contact time on sorption of Fe^{3+} by different clay samples.

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On the other hand, the investigated clay samples showed relatively low capacity to sorb Cu^{2+}. The results are presented in fig (9). From this fig ., it is observed that the maximum sorption of Cu^{2+} ranged from 41-75 %, for the studied clay samples, the equilibrium was attained after30 min., similar data was observed by other investigators (**Suraj, et. al., 1998**).

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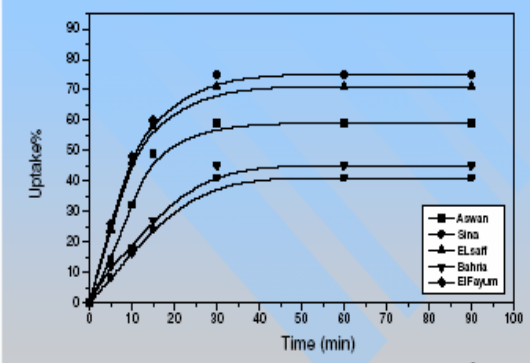

Fig(9):Effect of contact time on sorption of Cu^{2+} by different clay samples.

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Fig (10) Shows the variation of percent uptake of Zn^{2+} as a function of contact time. From this figure it is clear that clay samples collected from El-Fayoum and El-Saff have the highest sorption capacity towards Zn^{2+} since the % uptake ranged between 85-70%. Samples collected from Aswan, Bahryia and Sinai show a moderate capacity towards Zn^{2+} and the % uptake ranged between 48-31 %. This finding may be attributed to the chemical and mineralogical compositions of the investigated samples. (**Garcia, et. al., 1999**).

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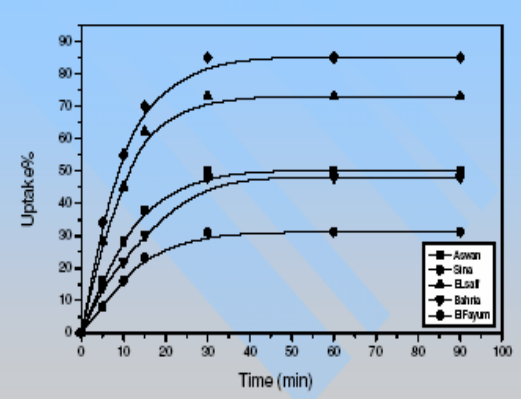

Fig(10):Effect of contact time on sorption of Zn^{2+} by different clay samples.

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Since the mineral content in each sample to other as well as shown in table (2). For example, the sample collected from El-Fayoum area have a different amount of kaolinite (5-15%), interstralified (25-40%) montmorillonite (>40%) and trace amounts of both illite, quartz and felspars minerals. In addition to the physical characterization of each mineral, such as the surface area, which may affect the sorption / desorption process of the investigated heavy metal ions by the studied clays. On other hand, the clay sample collected from Sinai which have the lowest percent up take have a large amount of kaolinite mineral (>40%) and trace amount of montmorilonite (<5%) in addition to about (25-40%) quartz.

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- The variation of the chemical composition of each sample are also affect the sorption process. Since the element content is varied as shown in table (4). From this table, it is clear that the SiO_2 content is varied from (65 to 48.2) for samples collected from El-Fayoum site and Sinai respectively. Also, the CaO content in this samples is ranged from 3.98 (El-Fayoum) to 0.25 (Sinai) which may affect the ion exchange between the investigated cation and Ca ions during the sorption process.

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Effect of PH

- Figures (11-14) show the effect of changing the pH of the aqueous phase on the uptake % of Pb^{2+}, Zn^{2+}, Fe^{3+} and Cu^{2+}. From these figures, it is clear that the uptake % of Pb^{2+} and Zn^{2+} showed a gradual increase by increasing the pH with a maximum values around the pH = 8-7.7 and then remain constant for both Pb^{2+} and Zn^{2+} respectively as shown in figs., (11, 12). On the other hand, the uptake % of Fe^{3+} and Cu^{2+} showed a relatively sharp increase by increasing the pH with a maximum values around 4.5 and then showed a slightly decrease until pH = 7 this is due to formation of hydroxide as shown in figs.(13, 14).

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•The general increase in the sorption capacity with increasing the pH of the media can be discussed in the light of the exchange properties of the hydrogen ions and their effect on the solubility equilibria with the different clay samples. Since the clay sample have exchange site of different binding energies, thus at low pH, the hydrogen competes for the available exchange sites and this negatively affects the uptake of the different cations. As the pH increases, the hydrogen ion concentration decreases and the competitive effect of the proton with the metal cations decreases with subsequent increase in the percentages of the uptake of the different cations. This explanation is in accordance with those given by other investigators. **(Rauf, et. al., 1999), (Helal, 1986).**

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Figure (11) shows the sorption of Pb^{2+} by the different clay samples at different pH values. It is clear that, the sorption of Pb^{2+} increases gradually with increasing pH of the medium. The uptake of the Pb^{2+} by the different samples was found to increase in the order:

El- Fayoum > El-saff > Aswan > Bahriya > Sinai

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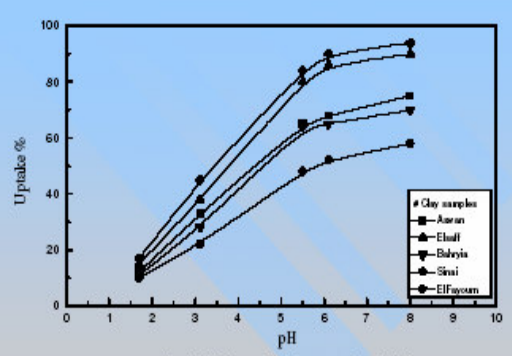

Fig.(11) Effect of pH on sorption ofpb^{2+} by different clays samples.

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- Figure (12) shows the relation between the uptake % and the final pH of the medium of Zn^{2+} sorbed by different clay samples. From this fig ., it is clear that the uptake % increases with increasing the pH. The sorption capacity of the different clay samples to sorb Zn^{2+} was found to increase in the following order:

EL-Fayoum > El-Saff >Aswan> Bahriya > Sinai.

The results obtained are in accordance with the findings of **(Papini et. al., 2002).**

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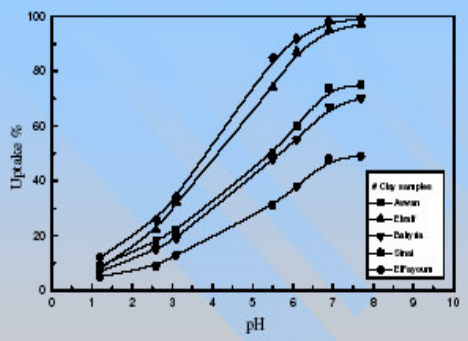

Fig.(12) Effect of pH on sorption of Zn^{2+} by different clay samples.

19

- Figures (13) and (14) show the sorption behavior of both Fe^{3+} and Cu^{2+} by the investigated clay samples at different pH values. From this figs, it is clear that the sorption of both element show a relative increases with increasing the pH until pH = 4.5 , followed by a slightly decrease until pH=7. The order of increasing the uptake % of Fe^{3+} and Zn^{2+} by different clay samples was found to follow the sequence :

El- Fyoum > El-Saff > Aswan > Bahriya > Sinai

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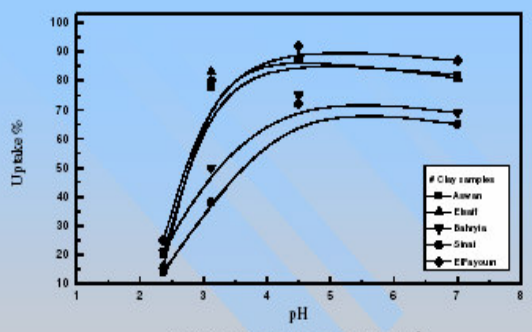

Fig.(13) Effect of pH on sorption of Fe^{3+} by different clays samples.

21

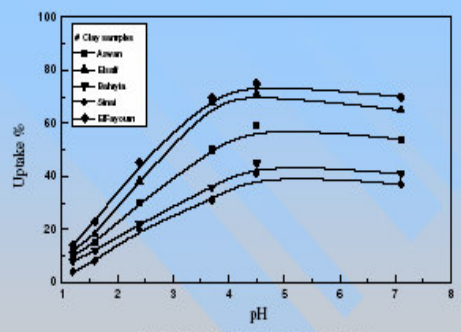

Fig.(14) Effect of pH on sorption of Cu^{2+} by Different clay samples.

22

•This may be attributed to the mineralogical and chemical composition of the investigated samples. From the mineralogical analysis table (3) it is shown that El-Fayoum clay sample have more than 40% of montmorillonite minerals that show high cation exchange capacity as it has been mentioned in table (1).

23

Adsorption Equilibria

- The rate of adsorption is controlled by transfer of species within the adsorbent particle because diffusion through solid is naturally slower than that in fluid. Therefore, the process continues until a characteristic equilibrium is attained. At equilibrium there is a defined distribution of solute between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process and is presented in the form of an adsorption isotherm. Also the process equilibrium indicates the adsorption capacity of adsorbent (clay) which is important to determine the usefulness and applicability of a mathematical model.

24

Single Component Adsorption systems

Adsorption isotherms

Adsorption isotherm were determined for the adsorption of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto different clays. The results are shown in Figs. (15), (16), (17) and (18) as plots of q_e(amount of metal removed) against C_e. The isotherms rise in the initial stages for low C_e (equilibrium concentration) and q_e values. This indicates that there are plenty of readily accessible sites. Eventually a plateau is reached in all the curves. Indicating the curvature of the isotherm, as it tends to a monolayer, as the C_e (equilibrium concentration) value increase considerably for small increase in q_e(amount of metal removed). This is possible due to the less active sites being available at the end of the adsorption processes as at Eq.(3-2).

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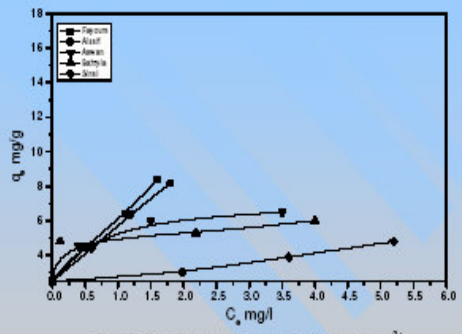

fig.(16) Equilibrium adsorption isotherm for Pb^{2+} onto clay samples.

26

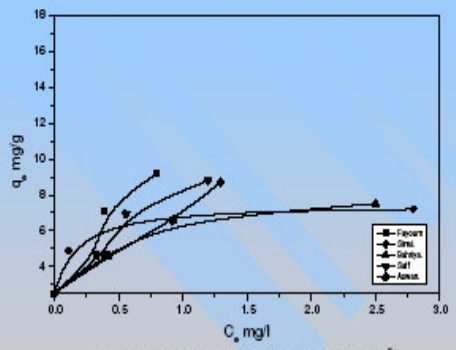

fig.(17) Equilibrium adsorption isotherm for Fe^{3+} onto clay samples.

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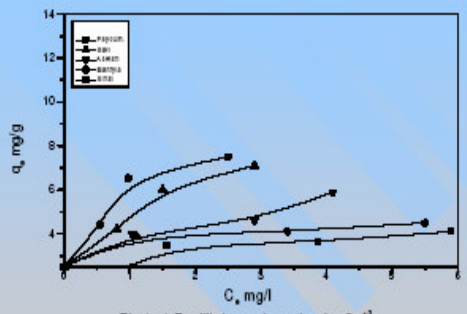


Fig.(18) Equilibrium adsorption for Cu^{+2} onto clay samples.

28

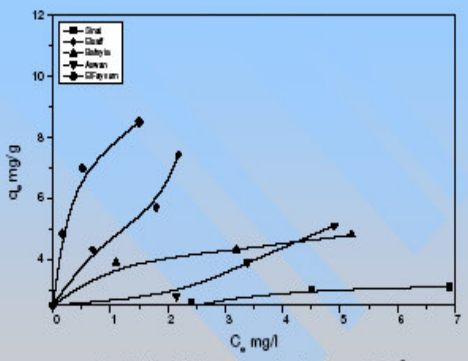
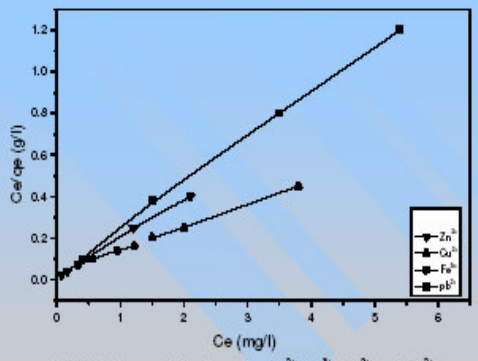


fig.(19) Equilibrium adsorption isotherm for Zn^{2+} onto clay samples.

29



Fig(19): Langmuir isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto El-Bahriya clay sample.

30

Isotherm analysis

- Several isotherm equations are available for this analysis. In this study two of these selected (a)The Langmuir and (b) Freundlich isotherms.

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(a) *Langmuir isotherm*

- The first isotherm tested was the Langmuir which is represented by Eq.(4 -1)

- $q_e = K_L C_e / (1 + a_L C_e)$ (4 -1)
- Eq (4-2) represents linear form convenient for plotting and determine the constants K_L and a_L .
- $C_e/q_e = (1/K_L) + (a_L/K_L)\, C_e$ (4 -2)

32

- The linear plots of C_e/q_e against C_e for Pb^{2+}, Fe^{3+}, Cu^{2+} ,and Zn^{2+} onto clay samples are shown in Figs. (19) , (20), (21), (22) and (23). The plot suggest the applicability of the Langmuir isotherm for the present systems, showing the formation of monolayer coverage of the adsorbate at the outer surface of adsorbent (panday et at., 1984). Fig (29-48) shows a comparison between experimental and theoretical data predicted by Langmuir isotherm for the adsorption of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto different clay samples. Which shows that there is an agreement between them. The values of K_L and a_L (Langmiur parameters) of the metals have been listed in Table (5,6,7,8). The values of K_L/a_L, represent the maximum adsorption capacity (q_{max}) of different clay samples for particular metal.

33

- The essential characteristics of Langmuir isotherm may be expressed in terms of a dimensionless equilibrium parameter R (Weber and Chakravorti, 1974), which is defined by:

$R = 1/(1 + a_L C_0)$ (4-3)

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- The parameter R. indicates the isotherm shape according to the following. R>1 unfavorable. R=1 linear. 0<R<1 favorable and R=0 irreversible. R values are incorporated in Table (5,6,7,8). they are in the range 0<R<1. Which means that the adsorbent chosen are favorable. Data from equilibrium studies Tables (9, 10, 11,12) proved that percentage removal of Pb^{2+} by using Sinai, El-Saff, Bahryia, El-Fayoum and Aswan. Ranged between 48 to 100% , 82 to 100%, 60 to 100%, 84 to 100% and 65 to 100% respectively for initial concentration ranged between 10 to 2.5 mg/l, and ranged between 72 to 100% , 88 to 100%, 78 to 100%, 92 to 100% and 87 to 100% for removal of Fe^{3+} respectively for the same range of concentrations. The percentage of Cu^{2+} removal was ranged between 41 to 77%, 71 to 100%, 45 to 100%, 75 to 100% and 59 to 100% for the same range of concentrations . The percentage of Zn^{2+} removal was ranged between 31 to 61% , 74 to 98% , 48 to 100%, 85 to 96% and 50 to 60% respectively for the same range of concentrations.

35

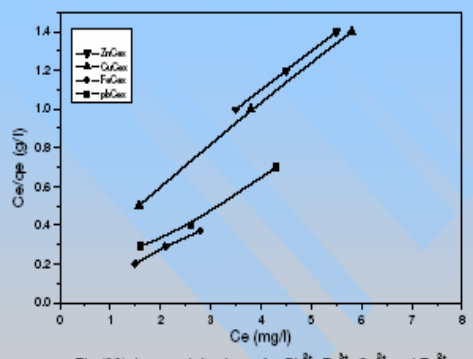

Fig.(20): Langmuir isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Sinai clay sample

36

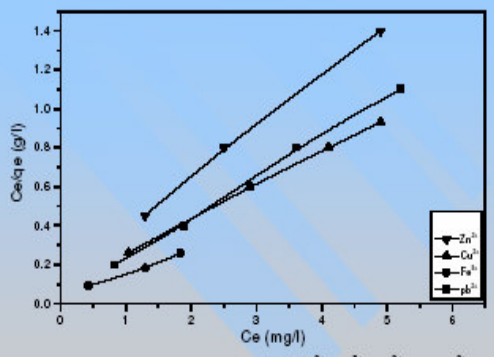

Fig. (21) Langmuir isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Aswan clay sample.

37

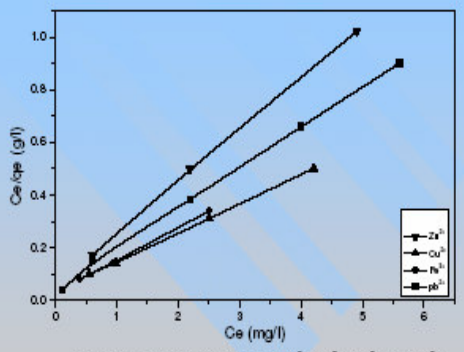

Fig.(22): Langmuir isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto El-Saff clay sample

38

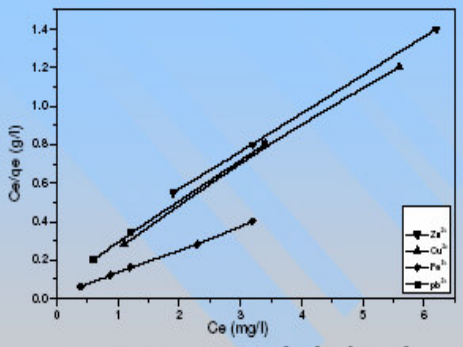

Fig.(23) Langmuir isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto El-Fayum clay sample.

39

Table (5) Langmuir constants for single adsorption systems.

Adsorbent	Pb^{2+}				
	K_L dm^3/mg	a_L dm^3/mg	$q_{max\ th}$ mg/g	R	r^2
El-Fayoum	13.02	2.77	4.6	0.43	0.999
Bahryia	33.35	7.2	4.63	0.23	0.999
Aswan	48.08	10.10	4.76	0.17	0.999
Sinai	49.92	7.8	6.4	0.16	0.999
El-Saff	25.84	4.00	6.46	0.28	0.999

40

Table (6) Langmuir constants for single adsorption systems.

Adsorbent	Fe^{3+}				
	K_L dm^3/mg	a_L dm^3/mg	$q_{max\ th}$ mg/g	R	r^2
El-Fayoum	73.42	8.77	8.37	0.11	0.9992
Bahryia	25.42	2.59	9.81	0.28	0.9986
Aswan	29.71	3.57	8.32	0.25	0.9999
Sinai	143.77	18.86	7.62	0.06	0.9998
El-Saff	35.14	4.36	8.05	0.22	0.9991

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Table (7) Langmuir constants for single adsorption systems.

Adsorbent	Cu^{2+}				
	K_L dm^3/mg	a_L dm^3/mg	$q_{max\ th}$ mg/g	R	r^2
Sinai	5.79	1.2	4.82	0.6	0.9998
El-Fayoum	14.72	3.03	4.8	0.410	0.9996
Elsaff	28.3	3.12	9.07	0.26	0.9999
Aswan	11.9	2.08	5.72	0.34	0.9998
El Bahryia	29.53	3.23	9.14	0.25	0.9999

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Table (8) Langmuir constants for single adsorption systems.

Adsorbent	Zn^{2+}				
	K_L dm^3/mg	a_L dm^3/mg	q_{max} ads mg/g	R	r^2
Sinai	3.33	0.66	5.04	0.75	0.9998
El-Saff	17.23	3.4	5.06	0.37	0.9998
El-Fayoum	5.86	1.16	5.05	0.01	0.9999
Aswan	7.90	2.08	3.79	0.55	0.9999
El Bahryia	85.64	16.12	5.31	0.10	0.999

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Table (12) Equilibrium data for single component system of Pb^{2+} with the different investigated clays.

Type	C_o mg/l	C_e mg/l	q_e mg/g	% Uptake
El-Fayoum	2.5	0	2.5	100
	5.0	0.5	4.5	90
	7.5	1.1	6.4	85
	10.0	1.6	8.4	84
El-Saff	2.5	0.0	2.5	100
	5.0	0.6	4.4	88
	7.5	1.2	6.3	84
	10.0	1.8	8.2	82
Aswan	2.5	0.0	2.5	100
	5.0	0.40	4.6	92
	7.5	1.5	6.0	80
	10	3.5	6.5	65
Bahryia	2.5	0.0	2.5	100
	5.0	0.12	4.8	96
	7.5	2.19	5.3	70
	10.0	4	6.0	60
Sinai	2.5	0.0	2.5	100
	5.0	1.9	3.02	60
	7.5	3.6	3.9	52
	10.0	5.2	4.8	48

V = 50ml , m = 0.05 g .

44

Table (13) Equilibrium data for single component system of Fe^{3+} with the different clay samples.

Type	C_o mg/l	C_e mg/l	q_e mg/g	% uptake
El-Fayoum	2.5	0.0	2.5	100
	5.0	0.33	4.6	93
	7.5	0.39	7.1	94
	10	0.8	9.2	92
El-Saff	2.5	0.0	2.5	100
	5.0	0.39	4.6	92
	7.5	0.56	6.9	92
	10.0	1.2	8.8	88
Aswan	2.5	0.0	2.5	100
	5.0	0.43	4.5	90
	7.5	0.92	6.5	88
	10.0	1.3	8.7	87
Bahryia	2.5	0.0	2.5	100
	5.0	0.39	4.6	92
	7.5	0.93	6.5	87
	10.0	2.5	7.5	75
Sinai	2.5	0	2.5	100
	5.0	0.113	4.88	97
	7.5	0.55	6.95	92
	10.0	2.8	7.2	72

V = 50ml , m = 0.05 g .

45

Table (14) Equilibrium data for single component system of Cu^{2+} with the different clay samples.

Type	C_o mg/l	C_e mg/l	q_e mg/g	% Uptake
El-Fayoum	2.5	0.0	2.5	100
	5.0	0.55	4.45	89
	7.5	0.98	6.52	86
	10.0	2.5	7.50	75
El- Saff	2.5	0.0	2.50	100
	5.0	0.8	4.20	84
	7.5	1.5	6.00	80
	10	2.9	7.10	71
Aswan	2.5	0.0	2.5	100
	5.0	1.04	3.96	79
	7.5	2.9	4.60	61
	10.0	4.1	5.90	59
Bahryia	2.5	0.0	2.5	100
	5.0	1.1	3.9	78
	7.5	3.4	4.1	54
	10.0	5.5	4.5	45
Sinai	2.5	0.57	1.93	77
	5.0	1.57	3.43	68
	7.5	3.87	3.63	48
	10.0	5.89	4.11	41

V = 50ml ,m= 0.05 g .

46

Table (15) Equilibrium data for single component system of Zn^{2+} with the different clays.

Type	C_o mg/l	C_e mg/l	q_e mg/g	% uptake
El-Fayoum	2.5	0.07	2.42	96.9
	5.0	0.16	4.83	96.6
	7.5	0.51	6.98	93.0
	10	1.5	8.50	85.0
ElSaff	2.5	0.03	2.47	98
	5.0	0.69	4.31	86
	7.5	1.8	5.70	76
	10.0	2.19	7.41	74
Aswan	2.5	0.98	1.52	60
	5.0	2.15	2.85	57
	7.5	3.39	3.90	52
	10.0	4.96	5.04	50
Bahryia	2.5	0	2.5	100
	5.0	1.1	3.9	78
	7.5	3.2	4.3	57
	10.0	5.2	4.8	48
Sinai	2.5	0.97	1.53	61
	5.0	2.40	2.60	52
	7.5	4.50	3.00	40
	10.0	6.9	3.10	31

V = 50ml , m = 0.05 g .

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(b) Freundlich isotherm

- he experimental equilibrium data for the adsorption of metals onto different clay samples have been analysed according to Freundlich isotherm shown by Eq. (4-4).
- $q_e = K_F C_e^{1/bF}$ (4 - 4)

Where:

- K_F : Parameter of Freundlish isotherm.
- b_F: Freundlish isotherm constant.
- A logarithmic plot linearizes the equation enabling the exponents b_F and K_F to be determined.
- $\log q_e = \log K_F + (1/b_F)\log C_e$ (4 - 5)

48

Figs (24-28) show the validity of equation (4-5) and the applicability of Freumndlich isotherm for adsorption of the study metal on the selected clays. the parameters K_F and b_F for metals have been calculated using the least squares method and are tabulated in Tables (13,14,15,16) show that the values of the Freundlich exponent, b_F, are greater than one. This indicates favorable adsorption by Sinai, El-Saff, Bahryia, El-Fayoum and Aswan. The study showed that EL-Fayoum clay sample has the highest adsorption capacity for all metal cations under investigation . The reason for this high capacity is due to presence of montmorillonite as a major constitute. This finding is in accordance with previous work for adsorption of high molecular weight of organic compounds (complex dyes) on montmorillonite clay (Treybal 1968), (Jain and Ram 1997), therefore EL-Fayoum clay was used as adsorbent in the column adsobe studies. (Nassar and EL-Geundi 1991), (Nassar 1998), (Nassar and Magdi 1997), (Nassar. et. al. 2000).

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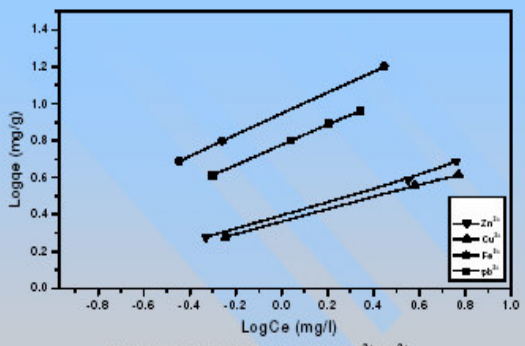

Fig. (24) Freundlich isotherm for Pb^{2+}, Fe^{2+}, Cu^{2+} and Zn^{2+} onto Sinai.

50

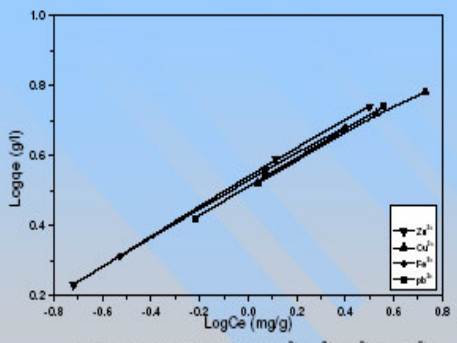

Fig.(25) Freundlich isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Fayum clay sample.

51

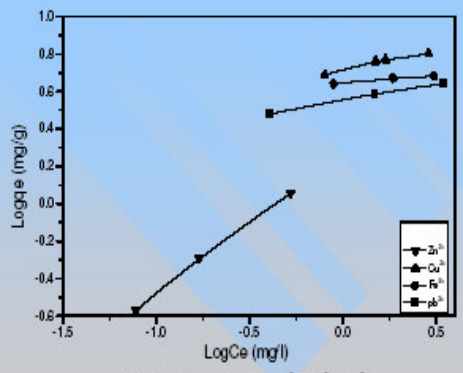

Fig.(26) Freundlich for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Bahria clay sample.

52

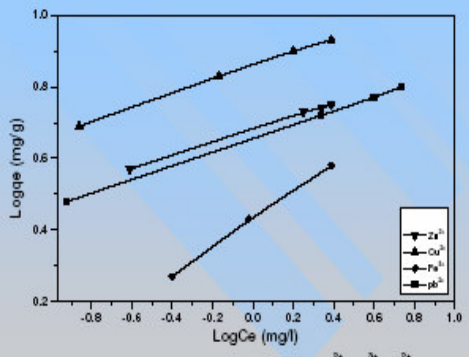

Fig. (27) Freundlich isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Al-Saff clay sample.

53

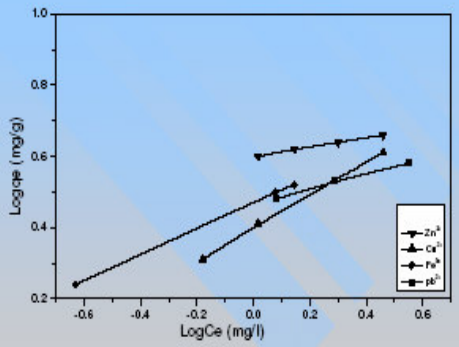

Fig. (28) Freundlich isotherm for Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} onto Aswan clay sample.

54

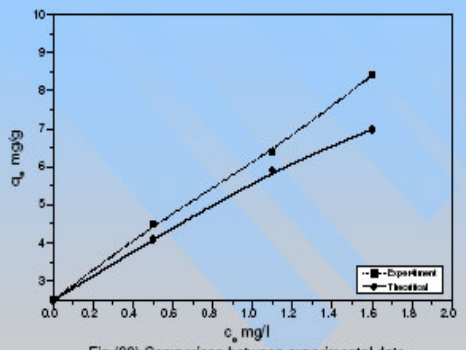

Fig.(30) Comparison between experimental data
and theoritically predicted extended
Langmuir isotherm for pb^{2+} onto El-Fayoum clay sample.

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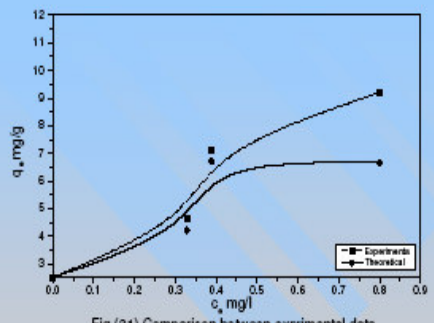

Fig.(31) Comparison between exprimental data
and theoritically predicted extended
Langmuir isotherm for Fe^{3+} onto El-Fayoum.

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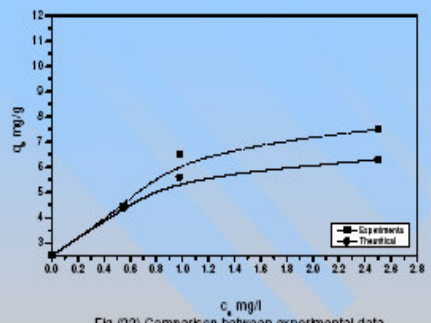


Fig.(32) Comparison between experimental data
and theoritically predicted extended
Langmuir isotherm for Cu^{2+} onto El-Fayoum clay sample.

57

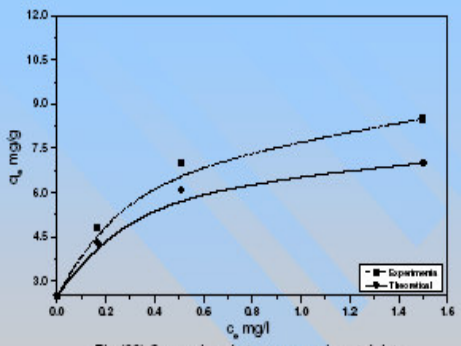
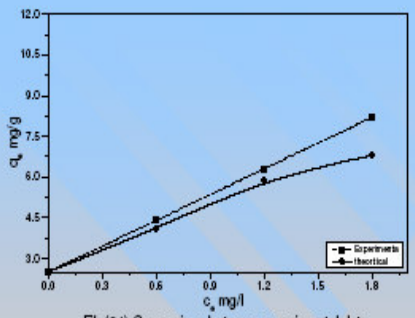


Fig.(33) Comparison between experimental data
and theoritical extended
Langmuir isotherm for Zn^{2+} onto El-Fayoum clay sample.

58



Fih.(34) Comparison between experimental data
and theoritically predicted extended
Langmuir isotherm for pb^{2+}onto El-Saff clay sample.

59

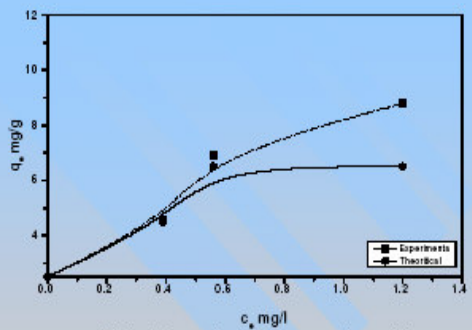


Fig.(35) Comparison between experimental data
and theoritically predicted
Langmuir isotherm for Fe^{3+} onto El-Saff.

60

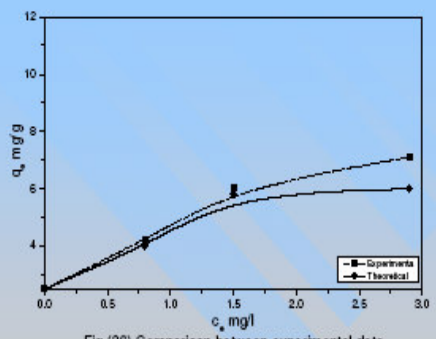


Fig.(36) Comparison between experimental data and theoritical perdicted extended Langmuir Isotherm for Cu^{2+} onto ElSaff clay sample.

61

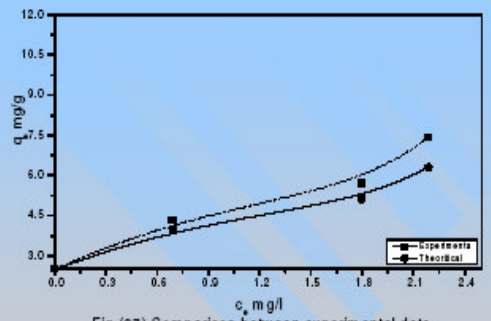


Fig.(37) Comparison between experimental data and theoritically predicted Langmuir isotherm for Zn^{2+} onto El-Saff clay sample.

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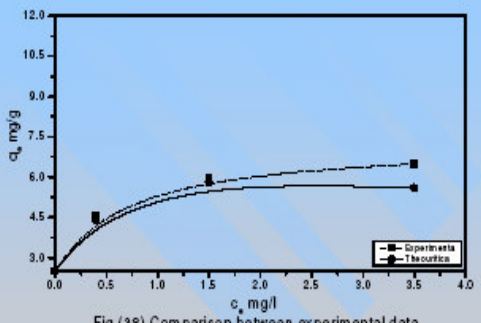

Fig.(38) Comparison between experimental data and theoritical predictedextended Langmuir isotherm for pb^{2+} Aswan clay sample.

63

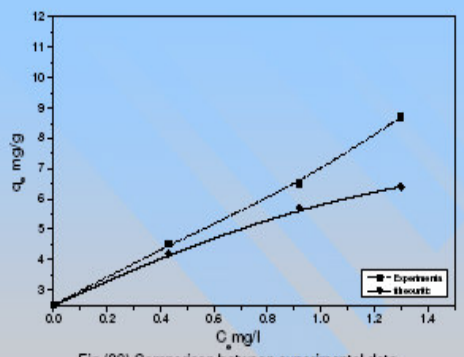

Fig.(39) Comparison between experimental data and theoritically predicted extended Langmuir isotherm for Fe^{3+} onto Aswan clay sample.

64

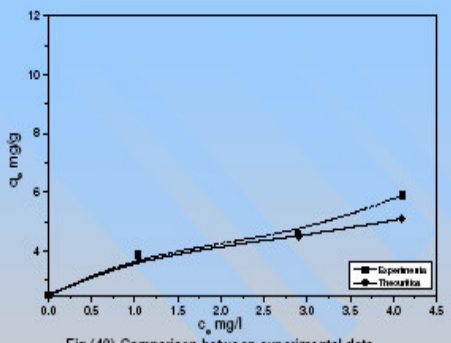

Fig.(40) Comparison between experimental data and theoritical predicted Langmuir isotherm for Cu^{2+} onto Aswan clay sample.

65

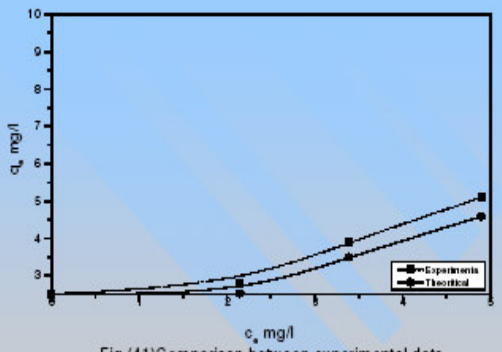

Fig.(41)Comparison between experimental data and theoritically pepredicted extended Langmuir isotherm for Zn^{2+} onto Aswan clay sample.

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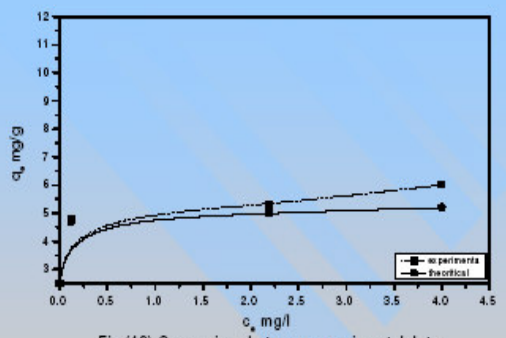

Fig.(42) Comparison between experimental data and theoritically predicted extended Langmuir isotherm for pb^{2+} onto Bahariya clay sample.

67

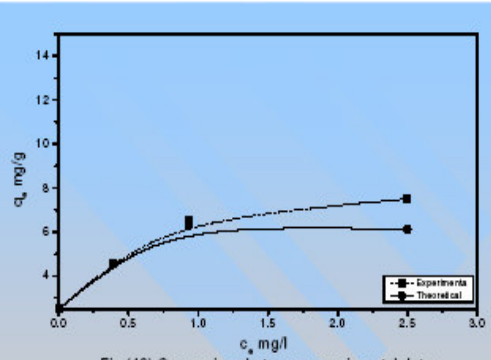

Fig.(43) Comparison between experimental data and theoritically predicted extended Langmuir isotherm for Fe^{2+} onto Bahariya clay sample.

68

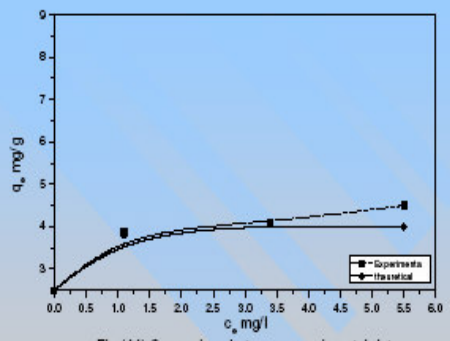

Fig.(44) Comparison between experimental data and theoritically predicted extende Langmuir isotherm for Cu^{2+} onto Bahriya clay sample.

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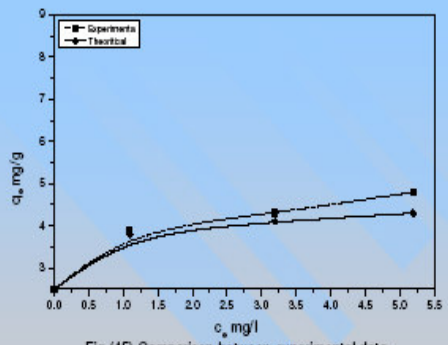

Fig.(45) Comparison between experimental data theoritically predited extended Langmuir isotherm for Zn^{2+} onto Bahriya clay sample.

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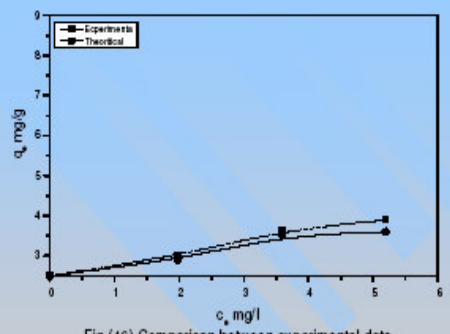

Fig.(46) Comparison between experimental data and theoritically predicted extended Langmuir osotherm forPb^{2+}onto Sinai clay sample.

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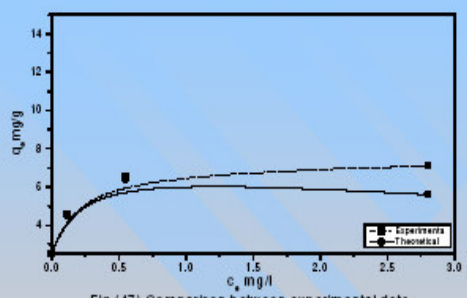

Fig.(47) Comparison between experimental data and theoritically predicted extended Langmuir isotherm for Fe^{3+} onto Sinai clay sample.

72

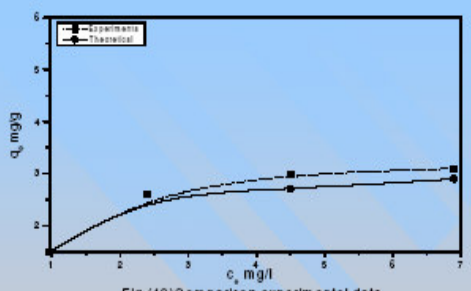

Fig.(49)Comparison experimental data and theoritical predicted Langmuir isotherm for Zn^{2+} onto Sinai clay sample.

73

Table (13) Freundlich constants for single adsorption systems.

Adsorbent	Pb^{2+}		
	K_F dm^3/mg	b_F dm^3/mg	r^2
El-Fayoum	5.97	1.84	0.9999
El-saff	4.52	5.21	0.9999
Aswan	3.54	5.74	0.9954
Bahryia	2.91	4.73	0.9982
Sinai	3.20	2.4333	0.9999

74

Table (14) Freundlich constants for single adsorption systems.

Adsorbent	Fe^{3+}		
	K_F dm3/m	b_F dm3/m	r^2
El-Fayoum	8.81	1.85	0.9999
Aswan	2.69	2.55	0.9991
Bahryia	4.415	13.24	0.9848
Sinai	2.94	2.75	0.9999
El- Saff	3.34	2.5	0.9999

75

Table (15) Freundlish constants for single adsorption systems.

Adsorbent	Cu^{2+}		
	K_F dm^3/mg	b_F dm^3/mg	r^2
Sinai	2.14	3.02	0.9996
El-Fayoum	7.21	5.18	0.9993
Aswan	5.19	5.00	0.9805
Bahryia	2.49	2.15	0.9996
El-Saff	3.10	2.63	0.9979

76

Table (16) Freundlich constants for single adsorption systems.

Adsorbent	Zn^{2+}		
	K_F dm^3/mg	b_F dm^3/mg	r^2
Bahryia	2.5	2.717	0.9987
El-Saff	4.78	5.55	0.9994
Sinai	1.55	1.52	0.9934
El-Fayoum	3.96	7.46	0.9988
Aswan	3.419	2.38	0.9996

77

Comparison between theoretical and experimental data.

Figs. (29) to (48) . show the comparison between theoretical and experimental data for adsorption of Pb^{2+} , Fe^{3+}, Cu^{2+} and Zn^{2+} onto Sinai, El-Safe, El-Fayoum, Bahryia and Aswan clay samples.

Equation (4-6) represents an extended Langmuir expression (Jain and Sonoeyink 1973), for multicomponent system based on the assumption that a certain amount of adsorption occurs without competition.

$$q_{ei}=K^0_{Li}C_{ei} / (1+\Sigma\, a^0_{Lj} / C_{ej}) \quad \text{.....(4-6)}$$

Where K^0_L and a^0_L are the single component isotherm constants.

Theoretical data in figs (29-48) was correlated using constant values of Langmuir K_L , a_L. There is some disagreement between theoretical and experimental data. This due to the competitive effect of components to adsorb on clay as well as the effect of metal- metal interaction at the adsorbent surface. The percent deviation was shown in table (17) .

78

Table (17): The percent deviation for all the investigated elements.

Element Sample	Pb^{2+}	Fe^{3+}	Cu^{2+}	Zn^{2+}
Sinai	12.5	9.8	19.2	20.5
El-Saff	20	13.3	11.8	19.4
Bahryia	12.2	6.5	11.25	11
El-Fayoum	20.9	10	13.6	18.9
Aswan	14.4	6.3	7.8	12.8

79

Effect of competing ion concentration

- The effect of changing the competing cation concentration on sorption of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} by the different clay samples was investigated. The obtained data were represented in figs. (50-53). Generally, it is observed that the presence of Ca^{2+} and Mg^{2+} ions as a competing cations decrease the uptake percent of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} by the investigated clay samples respectively.

- The effect of Ca^{2+} ions as a competing cation on sorption of Pb^{2+} by the investigated clay samples is shown in fig. (50), and the effect of Mg^{2+} ions as a competing cation on sorption of Fe^{3+}, Cu^{2+} and Zn^{2+} are shown in figs. (51,52,53). From this figures, it is clear that as the Ca^{2+} ions concentration increased up to 500 ppm, the uptake percentage of Pb^{2+} ions decrease by about 30%. The same observation for other cations, a decrease of uptake of Fe^{3+}, Cu^{2+} and Zn^{2+} due to presence of Mg^{2+} was noticed.

80

•This phenomena of competing action was recorded by other investigators **(Ezz El-Din, 1995)**, **(Murry and Murry 1973)** on studing the competing action of Ca^{2+}, Fe^{3+}, Na^{+} and K^{+} on the uptake of Co^{2+}. They attributed this effect due to the similarity of the ionic radii of the competing cation and the adsorbed cations, and also due to the high affinity of the competing ions for adsorption on clay than the investigation metals.

81

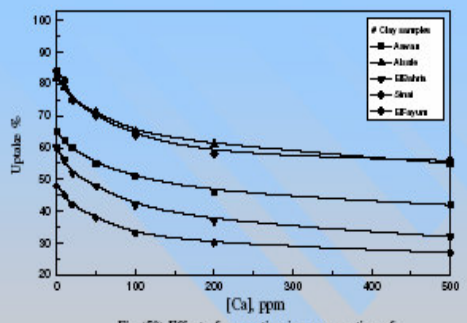

Fig.(50) Effect of competing ion on sorption of pb^{2+} by different clays samples.

82

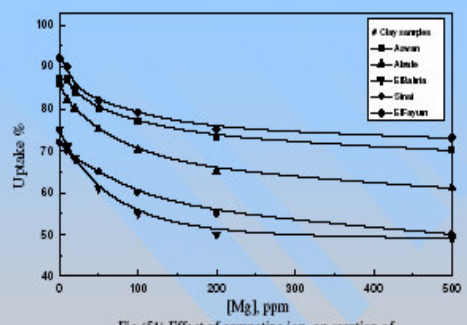

Fig.(51) Effect of competing ion on sorption of Fe^{3+} by different clays samples.

83

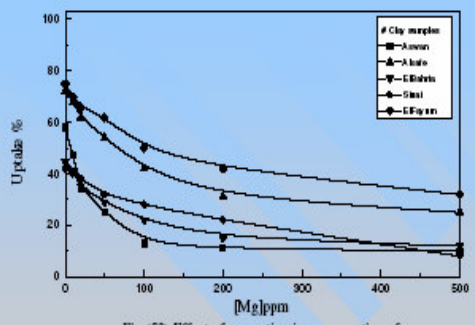

Fig.(52) Effect of competing ion on sorption of Cu^{2+} by Different clay samples.

84

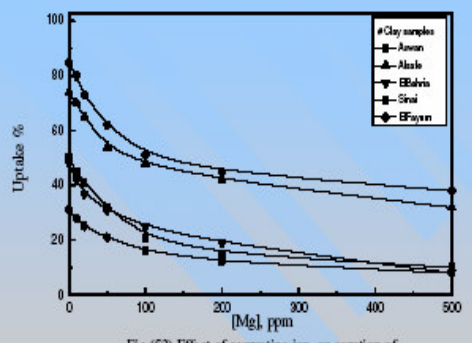

Fig.(53) Effect of competing ion on sorption of Zn^{2+} by different clay samples.

85

Desorption

- The study of desorption is similar, in many respects, to the adsorption methods. Desorption rate of heavy metals from clays is generally much less than the adsorption rate; such a study is usually carried out to find either the suitable conditions for the removal of an adsorption element from the clay surface or elucidation of the mechanism of preliminary adsorption, i e. determination of the nature of the sorption bond and / or the state of the trace element on the surface of the adsorbent.
- The desorption percent of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} is shown in table (20). The desorption data obtained after attained the equilibrium between the loaded samples and the leaching medium. **(Malakul, et. al. 1998), (Rogoshewski, et. al. 1983).**

86

•In case of Pb^{2+}, it is clear, from table (20), that the maximum desorption percent is in the range of 2 to 9 % for water , 1.3 to 9.4 % for $Ca(NO_3)_2$ and 24 to 83 % for 0.1N HCl and this is attained after nearly 60 min. The difference of the desorption percent may be attributed to the mineralogical and the chemical composition of each clay sample.

87

Table (20) : Desorption % of the investigated elements using different desorption solution

Element	Sample	Desorption%		
		H_2O	$Ca(NO_3)_2$	HCl
Pb^{2+}	Sinai	5.15	6.6	24
	El-Saff	3.98	5.3	38
	El-Bahriya	9	9.4	25
	Aswan	6	7.3	39
	El-Fayoum	2	1.3	83
Fe^{3+}	Sinai	4.1	4.5	26
	El-Saff	2.2	3.3	42
	El-Bahriya	5	6.2	28
	Aswan	3	4	45
	El-Fayoum	1	2	89
Cu^{2+}	Sinai	7.5	7.2	27
	El-Saff	5	6.1	41
	El-Bahriya	7.1	8.2	30
	Aswan	7	9	45
	El-Fayoum	4	5	90
Zn^{2+}	Sinai	6.2	7.5	28
	El-Saff	4.3	6.2	45
	El-Bahriya	8	9.5	35
	Aswan	5	6.3	48
	El-Fayoum	3	4	91

88

•In case of Fe^{3+}, it is shown in table (20), that the maximum desorption percent is in the range of 1 to 5 %for water, 2 to 6.2 % for $Ca(NO_3)_2$ and 26 to 89 % for HCl and is attained after about 60 min. El-Fayoum has the lowest desorption percent while El-Bahriya shows the highest. But the other clay samples have intermediate values. The variation in the desorption percent may be attributed to the differentiation in the nature of the clay samples.

89

•In case of Cu^{2+}, the variation of the desorption percent is shown in Table (20). It is observed that the desorption percent is in the range of 4 to 7.5 % for water, 5 to 8.2 % for $Ca(NO_3)_2$, 27 to 90 % HCl . after 60 min. El-Fayoum has the lowest desorption percent but the Sinai clay sample is the highest desorption percent for water and HCl. The desorption percent of the investigated clay samples has the following order:

Sinai >Bahriya >Aswan > El-Saff > El-Fayoum

•This sequence may be attributed to the nature of the adsorbent.

90

•In case of Zn^{2+} , the effect of contact time on desorption percent of Zn^{2+} is shown in table (20) . From the table it is clear that the desorption percent is in the range 3 to 6.2 % for water , 4 to 9.5 % for $Ca(NO_3)_2$ and 28 to 91 for HCl, this attained after 60 min. El-Fayoum is the lowest desorption percent but El-Bahriya has the highest. The desorption percent of the investigated clay samples has the following sequence:

Bahriya > Sinai > Aswan > El-Saff > El-Fayoum

•This may be attributed to the chemical and the mineralogical composition of the clay samples. This is finding in agreement with previous work (El-Said, 2000).

91

Column investigations

- From the previous studies it was found that, El-Fayoum clay sample gives higher adsorption capacity for all metal salts under investigations, therefore it is used for column investigation. The investigated clay was used as ion-exchangers for treatment of heavy metals wastes and other waste solutions. The solution is percolated through afixed bed of El-Fayoum clay operated down flow by running the solution through the exchanger from top to bottom.

92

•In column operation another expression was used for the filter capacity, known as breakthrough capacity, which is defined as the amount of ions taken up quantitatively by the column under the conditions in question. i.e. the number of mg/g which retained without any leakage observed.

93

• The breakthrough capacity is always lower than the total capacity of the column and is dependent upon a number of different variables, such as particle size, filtration rate and composition of solution. The following equation was used for the calculation of the sorption capacity of the column. **(Altin, et. al. 1999), (EL-Assy, et. al. 1993).**

$Q=(V_{50\%}-v).C_0/m$ (mg/g) (4-7)

Where,

Q : is the sorption capacity in mg/g.

C_0 : is the initial concentration in mg/l.

$V_{50\%}$: is the average breakthrough volume representing at C/C_0 50%

v : is the void volume (constant) ml.

m : is the mass of clay (g).

94

• The investigated clays resins can be used for the decontamination of liquid industerial wastes, specially the heavy metal ions, before discharge of the liquids to the environment . At the same time, it is one of the best methods of concentrating heavy metals and fixing them into clays. In this respect, the clays from El-Fayoum was investigated for the sorption of some heavy metal ions by using column techniqe.

• On the other hand , the breakthrough curves representing the uptake of Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} by the investigated clays are found in, Fig. (54).

95

Table (21) summarizes the breakthrough data and the sorption capacities of El-Fayoum clay for some heavy metals ions. From these data, it is clear the effectivness of the sorbent for the removal of the investigated elements from its solutions. However, the experiments should be extended to investigate the different other parameters as column high, column diameter and the effect of concentration of the influent …..etc. The preliminary data obtained by the used column in this investigation, however, are encouraging.

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Table (21): Breakthrough data and sorption capacity of El-Fayoum for some heavy metal ions

Element	C_0	El-Fayoum			
	ppm	Total Column Saturation Volume (ml)	Volume At C/C_0=50% (ml)	Breakthrough Volume (ml)	Capacity Q (mg/g)
Pb^{2+}	10	625	375	250	2.4
Fe^{3+}	10	525	225	175	1.7
Cu^{2+}	10	515	215	150	1.48
Zn^{2+}	10	450	120	50	0.48

97

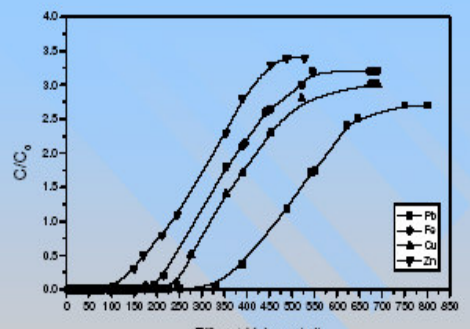

Fig.(54); Breakthrough curves of some heavy metal ions Pb^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+}

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RESULTS AND DISCUSSION

99

INDUSTRIAL WASTEWATER TREATMENT: METALS RECOVERY AND WATER RE-USE

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Abstract

Many industrial wastewater streams contain significant amounts of toxic metals (i.e. concentrations up to 500 mg/L or bigger) and should be treated before their discharge. Examples of wastewaters containing such metals are: 1) rinsing water in metal working enterprises (Cu, Ni, Zn, Sn, Cd, Pd, Ag, Al, Au, Cr, Mo etc.). 2) rinsing water in the semiconductor industry (Cu, Sn, Pb, Sb). 3) wastewater from the copper industry (As, Se (IV), Se (VI)). 4) treatment of mine water contaminated with different toxic metals (U, Ra, As, etc.), etc.

The conventional processes used to treat this kind of water (precipitation; precipitation/reduction; ion exchange/sorption bed filtration and the membrane processes: electrodialysis (ED), nanofiltration (NF) and reverse osmosis (RO) as well as process combinations (e.g. chemical precipitation and ion exchange; NF/RO and ion exchange; chemical precipitation and NF/RO and ion exchange etc)) have the following disadvantages:

1) high use of treatment chemicals 2) large quantities of sludge (solid waste) 3) inadequate selectivity 4) very slow bonding kinetics for the metals and their oxyanions (i.e. large capacity needed, high costs) 5) low capacity of ion exchangers and sorbents 6) insufficient metal removal 6) fouling and scaling problems in membrane operations. Usually, treatment of wastewater streams with large volume flow and high concentrations is needed which is not cost-effective.

It would be ideal if all the toxic metals could be separated from the wastestreams, the cleaned water reused and the metals recycled in concentrated form. It is not easy to achieve such a goal but most of it has been achieved in the framework of a European research project (METASEP) comprising 13 partners. The technology proposed comprised following treatment stages:

Step 1: selective bonding of toxic metal cations or oxyanions to suitable, selective bonding agents (BAs).
Step 2: Three variants a) separation of the formed BA-metal complexes by crossflow microfiltration / ultrafiltration (MF/UF) for wastewater with metal concentrations < 50 mg/l b) separation of the formed BA-metal complexes by a hybrid system of submerged MF membranes combined with flotation for wastewater with metal concentrations 50-500 mg/l and c) separation of the BA (produced on-site by electrocoagulation) and the metal complexes by MF for wastewater contaminated with problematic toxic metal anions (Se, As, Sb).

Step 3: recovery, regeneration and recycling of the BAs with simultaneous production of metal concentrates for re-use.
The project delivered an outstanding contribution to the key action 1.3.2 "Waste water treatment and re-use" of the Work Programme "Environment and Sustainable Development"

NATO/CCMS, 7-12 May 2006, Turkey

Industrial wastewater treatment: Metals recovery and water re-use

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School of Chemistry,
Lab. Gen. & Inorg. Chemical Technology
Thessaloniki, Greece

NATO/CCMS, 7-12 May 2006, Turkey

The problem

- Industrial wastewater streams contain significant amounts of toxic metals *(i.e. conc.up to 500 mg/L or higher)*

- *Should not be discharged without treatment*

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Examples

- metal working enterprises
  Cu, Ni, Zn, Sn, Cd, Pd, Ag, Al, Au, Cr, Mo etc.
- semiconductor industry
  Cu, Sn, Pb, Sb
- copper industry
  As and Se (IV) and Se (VI)
- mine water
  U, Ra, As, etc.
- ground drinking water
  As

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Available techniques

are not suitable for this kind of wastewaters

high volumes,
high conc. of metals

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METASEP proposal (FP 5)

- 13 European partners
  6 Academic institutions , 7 industries
- 3 Steps
- Outcome
  HYBRID flotation-MF/UF method
  European Patent

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- First Step
  selective bonding of toxic metal cations or oxyanions to suitable, selective bonding agents (BAs)

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- **Second Step (3 variants)**
  - a) For metal conc. < 50 mg/l : separation of the formed BA-metal complexes by crossflow microfiltration / ultrafiltration (MF/UF)
  - b) For metal conc. 50-500 mg/l : separation of the formed BA-metal complexes by a ***hybrid*** system of submerged MF membranes combined with flotation
  - c) For problematic toxic metal anions (Se, As, Sb) : separation of the BA (produced on-site by electrocoagulation) and the metal complexes by MF

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- **Third Step**
  recovery, regeneration and recycling of the BA's with simultaneous production of metal concentrates for re-use.

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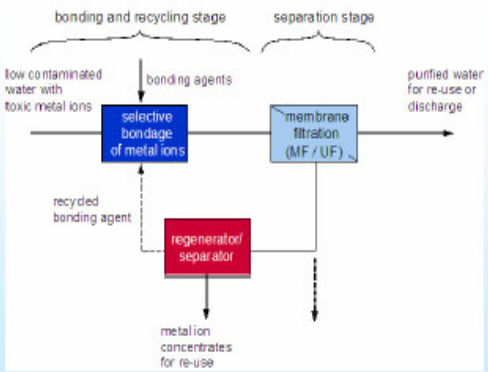
- **First Step**



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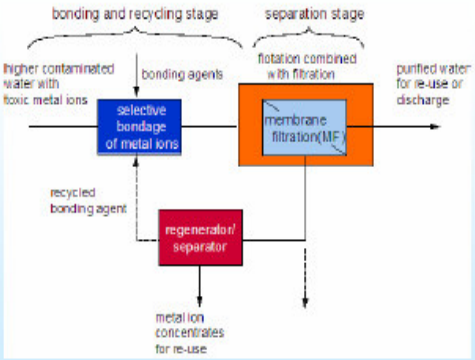
- **Second Step**



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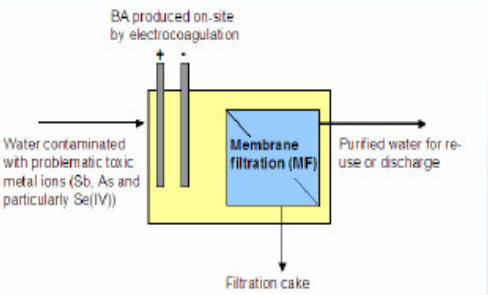
- **Third Step**



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AUTh Participation

- Development of Hybrid Flotation/MF system
- Optimization of its parameters

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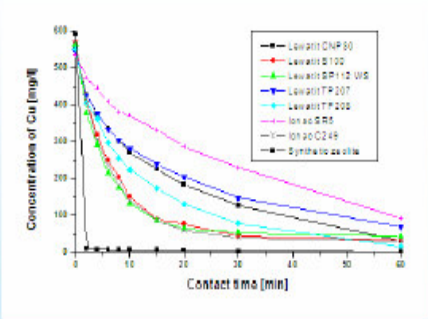
Bonding agent comparison



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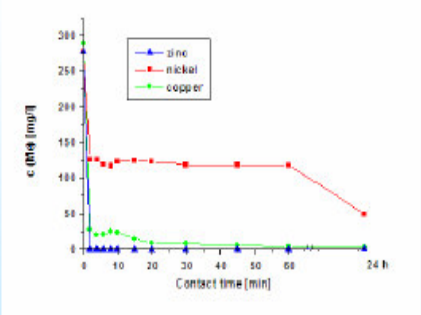
Competition by Mg^{+2}, Na^{+} (500 mg/L)



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membrane characteristics

Hybrid module with submerged ceramic multi-channel flat-sheet membranes (upt):

Membranes	Material:	ceramic
	Type:	multi-channel flat sheet
	Pore size:	0.3 µm
	Pure water flux:	3,000 l/(m²·h·bar)
Module design	Material of permeate collector:	polystyrene (PS)
	Sealing material:	epoxy
	Membrane arrangement:	3 in parallel
	Membrane distance:	20 mm
	Membrane geometry:	100 x 100
	Membrane area:	0.054 m² (3 x 0.018 m²)

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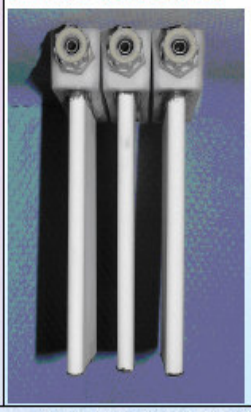
Module Plain view – Installed in cell



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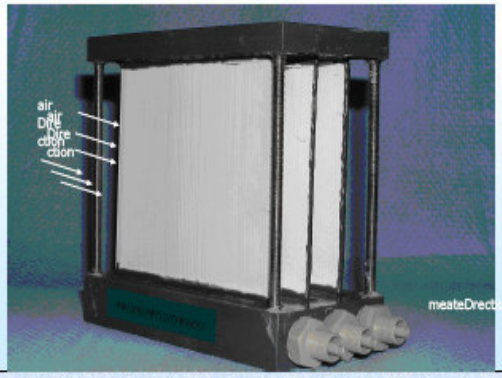
submerged module using polymeric multi-channel memb.



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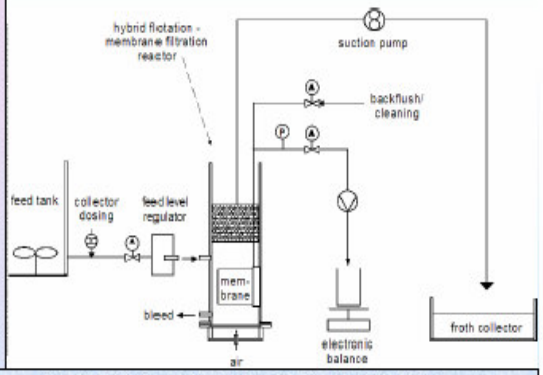
Pilot scale diagram



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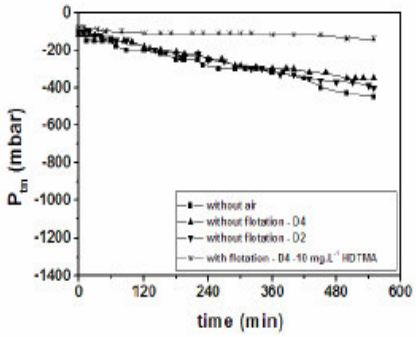
Comparison of membrane operation



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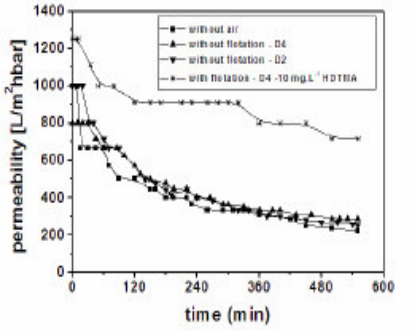

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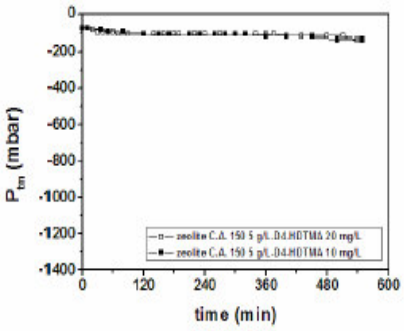
Hybrid membrane operation



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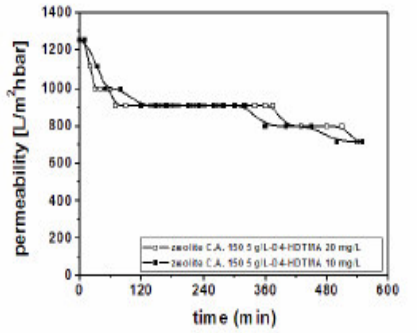
Comparison of membrane operation



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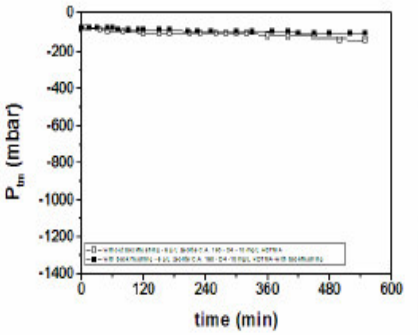
BackFlushing effect



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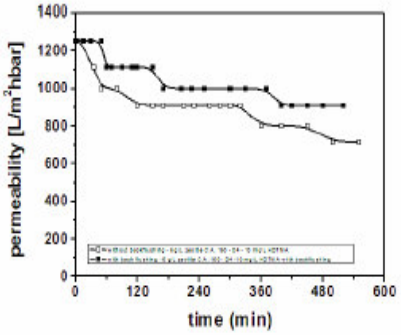

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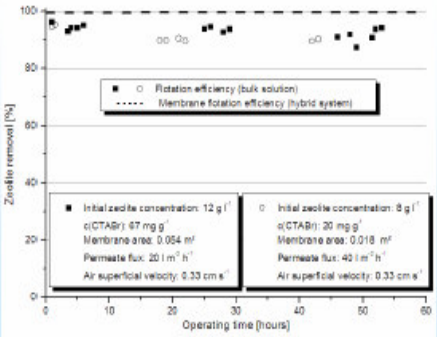
Hybrid cell: removal efficiency



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Conclusions

Hybrid cell

- Improved performance
- Improved energy efficiency
- Sensitive to changes in flotation efficiency

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Thank you for your attention

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WASTEWATER TREATMENT WITH INTEGRATED MEMBRANE-ELECTROFLOTATION METHOD

G.G. Kagramanov, V.A. Kolesnikov, P.S. Sudilovskiy

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Abstract

Research of wastewater treatment by combined membrane-electroflotation method was carried out. Integrated membrane-electroflotation machine combining co-current membrane flotation and counter-current electroflotation was designed. Air dispersion was realized in the tubular membrane saturator with the bubbling of air through ceramic microfiltration membrane to the water flow. The two-phase flow with gas content about 15-25% and average bubble size 0.5 mm was directed to the first chamber of flotation machine. The second chamber was designed for electroflotation polishing of membrane flotation effluent from the first one.

Influence of feed cation concentration and wastewater residence time on membrane-electroflotation rejection was studied. The rejection was stabilized on high level (95-97%) when feed cation concentration exceeds 30–50 ppm. The influence of residence time on the process rejection was determined. It was found that 10 minutes residence time is enough for 95% rejection of Fe^{3+}, Cu^{2+} and Ni^{2+} cations. Use of combined membrane-electroflotation method decreases energy consumption because of lower electric current is enough.

Experiments on microfiltration, nanofiltration and reverse osmosis treatment of flotation effluent were carried out to find the feed water pH dependence on rejection and membrane flux.

NF rejection is slightly smaller than RO one at pH 2–8 and becomes greater when pH<2. RO flux was dramatically decreased at pH<3 due to increasing of feed water osmotic pressure that means that RO cannot be applied to acidic cationic wastewaters with high osmotic pressure.

MF rejection is sufficiently high when pH is enough for cation hydroxide formation. NF and RO treatment can be applied if pH is acidic and all the cations are solved in water, on the contrary.

Provided the silt density index (SDI) is high, then membrane-electroflotation method can be applied for MF/NF pretreatment and MF/NF concentrate can be mixed with feed wastewater for cations rejection in flotation machine. If the SDI as well as pH values are low, then NF can be used in the first stage and concentrate can be treated by the integrated membrane-electroflotation method. The effluent can be recycled to the NF feed. Both of the methods can produce high-grade water and high-concentrated flotation froth as only waste, which can be dewatered and dried for utilization.

Keywords: Wastewater treatment, flotation, membrane filtration, MF, NF, RO

WASTEWATER TREATMENT WITH INTEGRATED MEMBRANE-ELECTROFLOTATION METHOD

Georgy G. Kagramanov, Vladimir A. Kolesnikov, Petr S. Sudilovskiy and Marina Frolova

Mendeleyev University of Chemical Technology of Russia, Moscow

INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

MEMBRANE FLOTATION

Membrane flotation is such a flotation process, where membranes are used for air bubbling.

Compared to dissolved air flotation (DAF), where air dissolved at high pressure is used for air bubbling and electroflotation, where DC current application to the water followed by electrolysis is used for H_2 and O_2 bubbles formation.

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MEMBRANE FLOTATION

- The most adequate bubbling rate dependence on gas content and average single bubbles floating rate (in static mode) is:

$$\frac{w}{w_0} = (1-\varphi)^{\frac{1-\varphi}{\varphi}}$$

- Optimal concentration of surfactant (SDS) is 7-8 ppm (in static mode)
- Optimal concentration of flocculant (PAA) is 2 ppm (in static mode)

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MEMBRANE FLOTATION

- The $Ni^{2+}/Cu^{2+}/Fe^{3+}$ rejection of membrane flotation is more than 99% (in static mode)
- Optimal pH for Ni^{2+} removal from the wastewater is 10.5 (in static mode)
- Optimal pH for Cu^{2+} removal from the wastewater is 9.5 (in static mode)
- Optimal pH for Fe^{3+} removal from the wastewater is 6.5 (in static mode)

INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

MEMBRANE FLOTATION

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- Optimal pH for Fe^{3+} removal from the wastewater is 6.5 (in static mode)

INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

MEMBRANE FLOTATION

Based on static membrane flotation experiments the run-time flotation unit with use of membranes for air bubbling was projected.

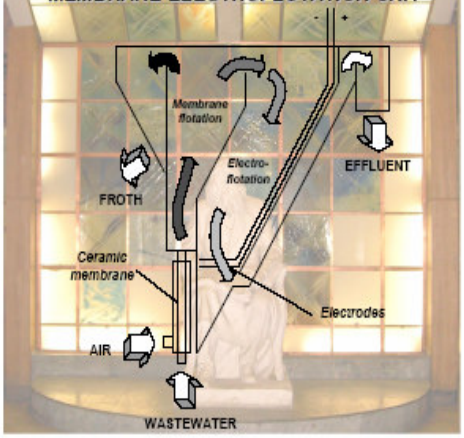
Air dispersion was realized in the tubular membrane module with the bubbling of air through ceramic MF membrane to the turbulent water flow.

INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

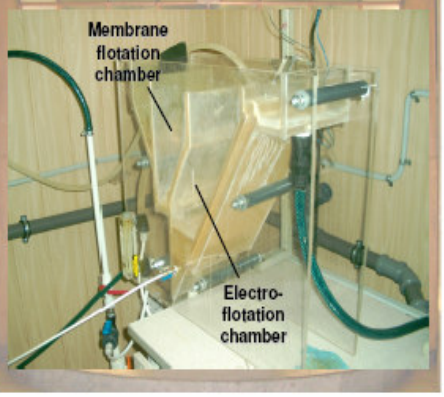
Integrated membrane-electroflotation machine combining co-current membrane flotation and counter-current electroflotation was designed.

The two-phase flow with gas content about 15-25% and average bubble size 0.5 mm is directed to the first chamber of flotation machine. The second chamber is designed for electroflotation polishing of membrane flotation effluent from the first one.

INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

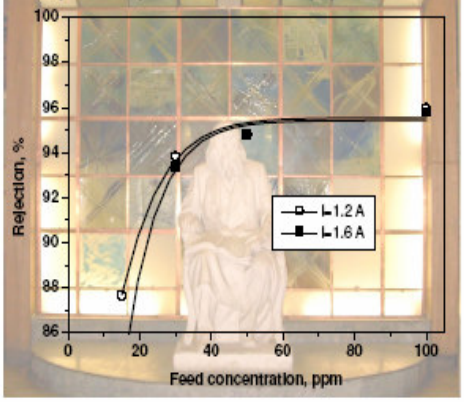


INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT



INTEGRATED MEMBRANE-ELECTROFLOTATION UNIT

Electric current and feed Fe^{2+} concentration influence



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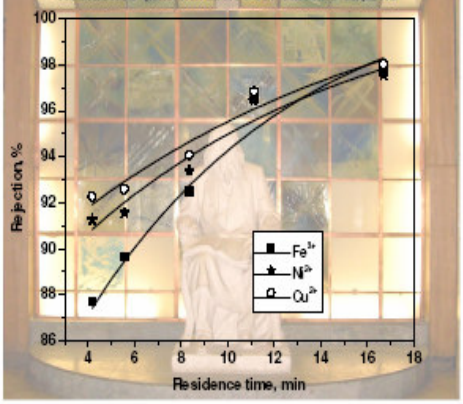
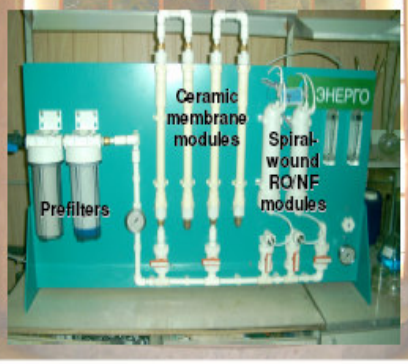
Residence time influence for various cations



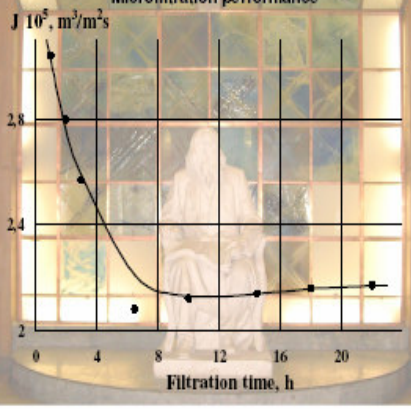
MEMBRANE FILTRATION POST-TREATMENT

Pilot unit for membrane filtration on ceramic MF/UF membranes and spiral-wound RO/NF membrane elements



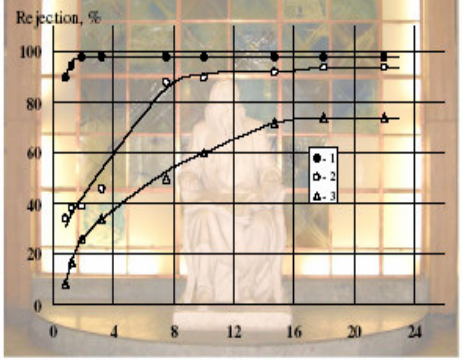
MEMBRANE FILTRATION POST-TREATMENT

Microfiltration performance



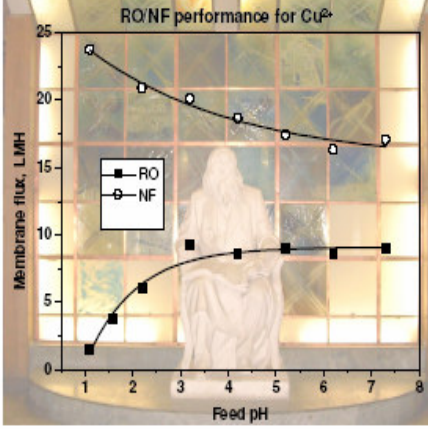
MEMBRANE FILTRATION POST-TREATMENT

Microfiltration performance



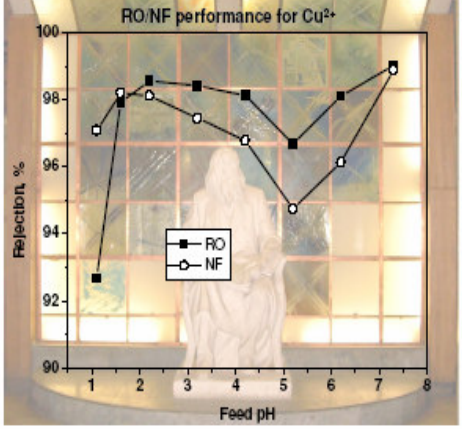
MEMBRANE FILTRATION POST-TREATMENT

RO/NF performance for Cu^{2+}



MEMBRANE FILTRATION POST-TREATMENT

RO/NF performance for Cu^{2+}



MEMBRANE FILTRATION POST-TREATMENT

MF rejection is sufficiently high when pH is enough for cation hydroxide formation. NF and RO treatment can be applied if pH is acidic and all the cations are solved in water, on the contrary.

The rejection minimum at pH=5 is accounting for isoelectric point of PA selective layer material.

NF rejection is slightly smaller than RO one at pH 2–8 and becomes greater when pH<2. RO flux was dramatically decreased at pH<3 due to increasing of feed water osmotic pressure that means that RO cannot be applied to acidic cationic wastewaters with high osmotic pressure.

CONCLUSIONS

➢If silt density index (SDI) is high, *membrane-electroflotation method can be applied for MF/NF pretreatment and MF/NF concentrate can be mixed with feed wastewater for cations rejection in flotation machine*

➢If the SDI as well as pH values are low, *NF can be used in the first stage and concentrate can be treated by the integrated membrane-electroflotation method. The effluent can be recycled to the NF feed.*

➢Both of the methods can produce high-grade water and high-concentrated flotation froth as only waste, which can be dewatered and dried for utilization.

Thank you for your attention
Questions?

APPLICATION OF NEW INDEXES FOR COMPARING MEMBRANE OPERATIONS TO TRADITIONAL TECHNIQUES

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[1,2] *Department of Chemical Engineering and Materials, University of Calabria, Via Pietro Bucci Cubo 17/C, 87030 Rende (CS) Italy (e.drioli@itm.cnr.it)*

Abstract

The application field of membrane units is continuously growing, also thanks to the development of new membrane systems, such as membrane contactors, that are able to carefully control the gas content in aqueous streams [1, 2] and that allow to achieve very high removals in the purification of both gaseous and aqueous phases [3].

In order to establish the convenience in using membrane operations instead of conventional ones, it is important to have "terms of reference" to consider in the evaluation. The development and the application of "indexes for comparison" is, therefore, of high interest to perform the choice.

In this contribution new proposed indexes (Productivity/Size ratio; Productivity/Weight ratio; Environmental Impact; Flexibility; Modularity) are used to compare the performance of membrane units with that of traditional devices for a case study: the sparkling water production.

References

1. A. Gabelman & S.-T. Hwang. 1999. Hollow fiber membrane contactors. J. Membr. Sci. 159: 61-106.
2. A. Criscuoli, E. Drioli, U. Moretti. 2003. Membrane contactors in beverage industry for controlling the water gas composition, in *Advanced Membrane Technology*, editors: E. Drioli, G.G. Lipscomb, and W.S.W. Ho, *Annals of New York Academy of Sciences*, New York, USA 984: 1-16 ISBN: 1-57331-427-7
3. E. Drioli, A. Criscuoli, E. Curcio. 2006. Membrane contactors: fundamentals, applications and potentialities. ISBN: 0-444-52203-4, Elsevier, Amsterdam

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Application of new indexes for comparing membrane operations to traditional techniques

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Aim of work

To use new proposed indexes (Productivity/Size ratio; Productivity/Weight ratio; Environmental Impact; Flexibility; Modularity) to compare the performance of membrane units with that of traditional devices for a case study: the sparkling water production.

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Methodologies used for comparing membranes with traditional operations

-Exergy analysis;

-Substitution coefficient;

-Green metrics

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Exergy analysis

The convenience of an innovative process with respect to the traditional one can be evaluated in terms of exergetic efficiency of the process by calculating the entropic losses (or production of entropy).

The exergy destroyed in entropy production corresponds to a lower work obtained or a higher work required.

The exergy analysis helps in identifying the parts of the plant less efficient.

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Substitution coefficient (CS)

Since membrane operations utilise in prevalence electrical energy, the estimate benefit can be done using the substitution coefficient which compares the primary energy *(energy supplied by fuel combustion to produce thermal energy)* saved to the electrical energy consumed in cycles that utilise electricity-consuming operations in substitution of conventional thermal operations.

The substitution results convenient when the CS is greater than 10.5 MJ/kWh (2.5 Mcal/kWh)

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Green metrics

Mass intensity = Total mass (kg)/ Mass of product (kg)

Energy efficiency = Total process energy/ Mass of product (kg)

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New proposed indexes for comparison (1)

$$\text{PS (productivity/size ratio)} = \frac{\text{P/Size (membranes)}}{\text{P/Size (traditional)}}$$

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New proposed indexes for comparison (2)

$$\text{PW (productivity/weight ratio)} = \frac{\text{P/Weight (membranes)}}{\text{P/Weight (traditional)}}$$

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New proposed indexes for comparison (3)

$$\text{EI} = \frac{\text{P/Load of pollutant emissions(membranes)}}{\text{P/Load of pollutant emissions(traditional)}}$$

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New proposed indexes for comparison (4)

$$\text{Flexibility1} = \frac{\text{Variations}_{\text{handled}}\text{ (membranes)}}{\text{Variations}_{\text{handled}}\text{ (traditional)}}$$

Ability to handle variations that might occur during the life of the plant

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New proposed indexes for comparison (5)

$$\text{Flexibility2} = \frac{N_{\text{processes able to satisfy}}\text{ (membranes)}}{N_{\text{processes able to satisfy}}\text{ (traditional)}}$$

Ability to be applied in different cycles of production

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New proposed indexes for comparison (6)

$$\text{MI (modularity index)} = \frac{\text{Productivity}_2\text{ (scale up)}}{\text{Productivity}_1}$$

$$\text{M (modularity)} = \frac{|\text{Area}_2/\text{Area}_1\text{ (membranes)} - \text{MI}|}{|\text{Volume}_2/\text{Volume}_1\text{(traditional)} - \text{MI}|}$$

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Case study: the sparkling water production

Feed stream

Water flow rate, 30 m^3/h

T, 20 °C

O_2 content: 9.24 ppm (saturation value)

Exit stream

Water flow rate, 30 m^3/h

T, 20 °C

O_2 content: less than 0.05 ppm

CO_2 content: around 4.3 g/L

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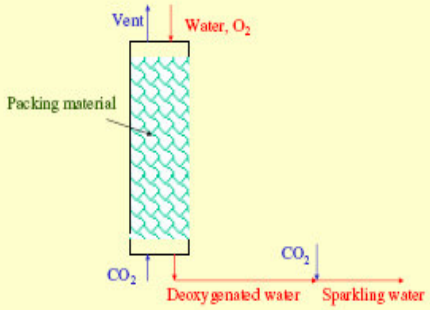
Sparkling water production – traditional system



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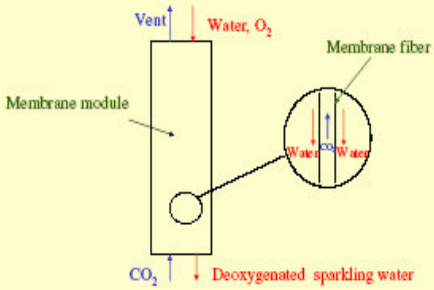
Sparkling water production – membrane system



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Sparkling water production – traditional system

CO_2 flow rate (kg/h)	130
Vent (kg/h)	3
Size (m^3)	1.55
Weight (kg)	700

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Sparkling water production – membrane system

CO_2 flow rate (kg/h)	110
Vent (kg/h)	3
Size (m^3)	0.24
Weight (kg)	300

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Sparkling water production, traditional - membrane system comparison (1)

PS	6.4
PW	2.28
EI	1
Mass intensity ratio	0.85

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Sparkling water production : traditional - membrane system comparison (2)

Variations in the operating conditions considered:

- Water temperature from 20°C to 5 °C
- Water flow rate +-50% (from 45 m^3/h to 15 m^3/h)
- Oxygen content in the water (at 20°C, from 9.24 ppm to 1 ppm)

Flexibility1 → 1.39

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Sparkling water production: traditional - membrane system comparison (3)

The traditional system could be also applied to:
- liquid-liquid operations.

The membrane system can be also applied to:
- liquid-liquid operations;
- liquid-vacuum operations;
- gas- vacuum operations;
- membrane/osmotic distillation.

Flexibility2 → 4

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Sparkling water production: traditional - membrane system comparison (4)

Volume of traditional system for treating 30 m^3/h → 1.55 m^3
Volume of traditional system for treating 3 m^3/h → 0.098 m^3

Area of the membrane system for treating 30 m^3/h → 390 m^2
Area of the membrane system for treating 3 m^3/h → 38 m^2

Modularity → 0.054

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Conclusions

For the *case study* analyzed, the membrane system results to be more convenient in terms of:

- mass intensity;
- size;
- weight;
- ability to handle variations;
- ability to be applied in different operations;
- modularity.

A. Criscuoli and E. Drioli

ARSENIC REMOVAL FROM WATERS USING MAGNETICALLY MODIFIED ZEOLITE

Miroslava Vaclavikova, George Gallios, Marek Matik, Stefan Jakabsky and Slavomir Hredzak

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Abstract

Water is very limited natural source and in many cases there is no enough water supply of appropriate quality for industrial and domestic use. Many pollutants in water streams have been identified as toxic and harmful to environment and human health. Among them arsenic is considered as high priority one. It occurs naturally in rocks and soils, water, air, plants, and animals. Volcanic activity, the erosion of rocks and minerals, and forest fires are also sources that can release arsenic into the environment. Anthropogenic activities are also responsible for arsenic release into the environment. Wood preservatives, paints, drugs, dyes, metals, and semi-conductors contain arsenic. Agricultural applications, mining, and smelting contribute to arsenic releases as well. Arsenic has been found at higher levels in underground drinking water sources then in surface waters. Several reports have been widespread of arsenic poisoning e.g. Bangladesh, West Bengal, India, etc. Most of arsenic in drinking water is in inorganic form either as As(III) or As(V). Several studies have linked long-term exposure to arsenic contamination with cancer and cardiovascular, pulmonary, immunological, neurological, and endocrine effect. EU and USA authorities have set new maximum contaminant level (MCL) for arsenic in drinking water, which was dropped from 0.005 μg/L to 0.001 μg/L. It is believed that with new standards around 5000 community water systems of the 74.000 in total would meet to take corrective actions to lower arsenic level in drinking water. 94% of these water systems serve fewer than 10.000 people each.

Arsenic contamination is a worldwide problem and become a challenge for world scientists. A variety treatment processes have been studied for precipitation-coagulation followed by filtration, lime softening, reverse osmosis, electrodialysis, nanofiltration, ion exchange and sorption. Even though that these techniques are effective, it is difficult to achieve the required limit. Sorption/surface precipitation on iron oxides based materials has been found to be effective in removing both As(III) and As(V) as well. These sorbents can be easily synthesized and possess fairly uniform chemical and physical properties. As they are usually nano-structures, which is significant disadvantage for the solid liquid (S/L) separation after the sorption process. The scope of this research is to incorporate Fe-oxide based nanomaterials into a well-organized host matrix. Nanoporous and microporous crystals, such as molecular sieves (zeolites) are ideal hosts for accommodation of organic and inorganic molecules, polymeric chains, etc. due to their uniform pore size and their ability to sorb molecular species.

Iron oxide based magnetic nanoparticles were synthesized by co-precipitation of Fe(III) and Fe(II) in the presence of zeolite–clinoptilolite (40-60%) with particle size 0.042-0.09 mm. The new magnetic zeolite was tested for the removal of As species from model aqueous solutions, which shows the sorption capacity for arsenic of about 50 mg/g of sorbent.

Presented research was supported by Science and Technology Assistance Agency under the contract No. APVT-51-017104 as well as by NATO Collaborative Linkage Grant EST.EAP.CLG 981103.

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Arsenic Removal from Waters Using Magnetically Modified Zeolite

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NATO CCMS – Clean Products and Processes, Istambul, Turkey, 2006

Causes

- *Arsenic* - recognized as a major problem for many parts of the world;
- enters the environment through both natural and anthropogenic sources (metallurgical, glassware, mining, ceramic industry, etc.);
- the new maximum contaminant level (MCL) of arsenic in drinking water in EU (98/83/EC) and USA has been set to 10 µg/L.

Research Overview

Synthesis of Magnetite Fe_3O_4 ($FeO.Fe_2O_3$)

$Fe^{2+} + Fe^{3+} + OH^- \rightarrow Fe_3O_4 \rightarrow \gamma\text{-}Fe_2O_3$ (in the case of oxidation)

Material Study

- Chemical and mineral composition
- TEM/SEM measurements → 10-40 nm → 20-900 nm (aggregation)
- Surface area measurements → 84.1 m^2/g
- Zeta potential measurements → PZC at pH 6.5
- Magnetic susceptibility → ferromagnetic

Sorption study

- Batch type study

Sorption Study

- Batch type study

C_{init}= 20-200 mg/L

C_s = 2 g/L

pH = 3.5

Temperature … ambient 22±1°C

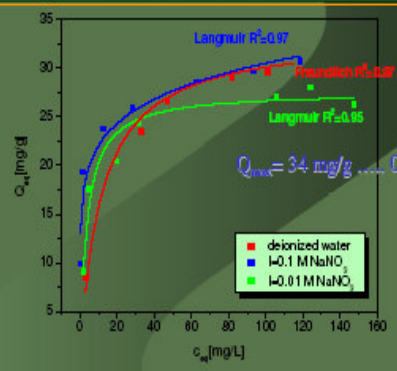
Ionic strength ….. H_2O, 0.01, 0.1 M $NaNO_3$

- Sorption isotherm constructions

Freundlich (parameters … K, b, R^2)

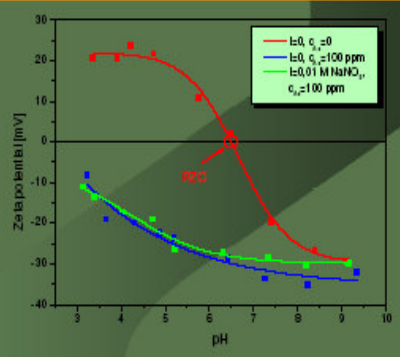
Langmuir (parameters …., Q_{max}, K, R^2)

Sorption Study



b= 0.31 …. 1/b=3.2, so ca. 3 arsenic molecules per surface site are sorbed

Zeta Potential



→ Specific sorption

!!! Problems !!!

Iron nano-sorbents – big surface size … good sorption capacity, but difficult S/L separation.

? Solution ?

If sorbent is magnetic – easy S/L separation in magnetic field.

Incorporation of iron oxide based nano-particles into the pores of zeolite crystals

modification of zeolite surface

- creating localized functional groups with a good affinity to inorganic anions, while retaining their affinity to cations as well.

Magnetic Zeolite

Zeolites

- are ideal hosts for accommodation of organic and inorganic molecules, because of their uniform pore size and their ability to adsorb molecular species;
- are known as good sorbents of cations and the modification of their surface can create localized functional groups with a good affinity to inorganic anions as well.

Magnetic Zeolite

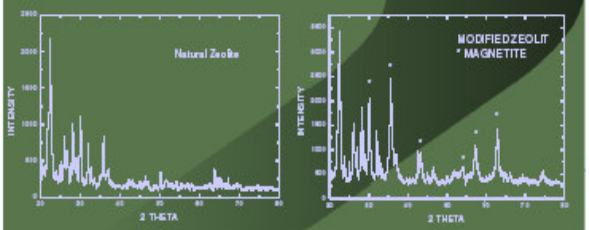
Material Preparation

- co-precipitation of Fe(III) and Fe(II) in the presence of zeolite
- Zeolite – clinoptilolite (40-60%) Nizny Hrabovec, Slovakia;
  - particle size 0.042-0.09 mm
- Zeolite:magnetite = 5:1

  Reaction Ratio …. Fe(III):Fe(II)=2

  Temperature …. 35°C; N_2 atmosphere
- New magnetic material has been produced …. Fe_{TOTAL}=7.81%, Fe(II)=0.39 % (15% magnetite, 85% maghemite)

Material Characterization

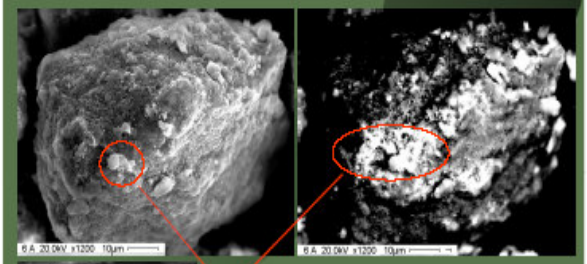


Properties	Natural Zeolite	Modified Zeolite
Surface area [m^2/g]	22,17	34
Magnetic susceptibility [SI units]	0,77 . 10^{-3}	0,14

Paramagnetic

Mag. susceptibility of magnetite …. 0.6 SI Units ….. Ferromagnetic

Material Characterization



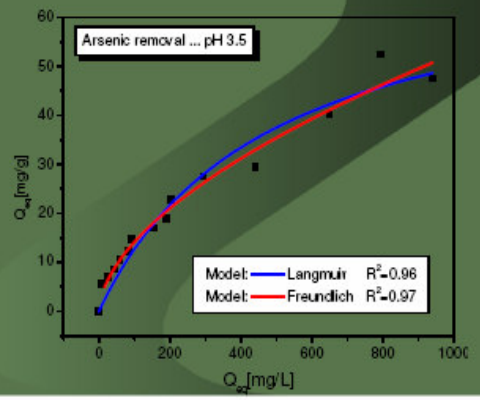
Fe

Mössbauer spectroscopy

58% of iron nanoparticles are inside zeolite structures

Magnetic Zeolite

Sorption Study



Conclusion

- New efficient sorbent has been developed
- Easy S/L separation using high gradient magnetic field (magnetic filtration)
- Challenge for using in dynamic (column) studies

Acknowledgement

- NATO Collaborative Linkage Grant EST.EAP.CLG 981103 (IGT SAS, Slovakia & AUTH, Greece)
- Science and Technology Assistance Agency – Program for young aid APVT-51-017104

COLOR REMOVAL FROM TEXTILE WASTEWATERS BY CHANGING THE SURFACE PROPERTIES OF ADSORBENT MATERIAL

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Abstract

Most industries use dyes and pigments to color their various products. Use of color for textile product is very common. However, the removal of color from textile mill effluents has been a major problem for many years. Many dyes are inert and non-toxic at concentrations discharged into the receiving bodies. However, color in the water is very undesirable. Some dyes are harmful to the aquatic life because they contain highly toxic metal complexes.

A low-cost basaltic tephra and clinoptilolite were used for the adsorption of basic and acidic dyes from aqueous solutions.

The experiments were conducted to determine adsorption capacities of natural and modified adsorbents that were basaltic tephra and clinoptilolite on some dyestuffs used in textile industry. Different particle sizes of natural basaltic tephra and clinoptilolite were tried in order to investigate the adsorption of basic and acidic blue dyestuffs from an aqueous solution to see the effect of particle size on adsorption process. Adsorption isotherms for different particle sizes of basaltic tephra and clinoptilolite were obtained. It is seen from the results that the smallest size particles have the maximum adsorption capacity as expected due to their higher surface area on which the adsorption takes place.

Adsorption isotherms for different particle sizes were analyzed according to the Langmuir and Freundlich isotherm equations. It is seen that Langmuir equation represents the adsorption isotherm better than the Freundlich isotherm equation.

The surface characteristics of the adsorbants were changed by using HTAB. Natural basaltic tephra has higher adsorption capacity than that of modified tephra. Prior to modification, attractive forces between basic dyes, which are cationic dyes, and natural adsorbent, of which surface charges are negative, were dominated. With the modification, the surface charges of the natural basaltic tephra were changed from anionic to cationic, i.e. electrostatic forces between the surface of adsorbent and dyestuffs were changed. Therefore, adsorption capacity of tephra was decreased. Under the same experimental conditions, the experiments were repeated with clinoptilolite. The reverse effect was obtained with the clinoptilolite. The adsorption capacity of clinoptilolite was increased.

Adsorption capacities of natural clinoptilolite and its modified form for basic and acidic dyestuffs seemed to be very promising.

METU, Ankara, Turkey

COLOR REMOVAL FROM TEXTILE WASTEWATERS BY CHANGING SURFACE PROPERTIES OF ADSORBENT MATERIAL

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1

INTRODUCTION

- Adsorption process has been found to be superior to other chemical techniques for removal of dyes from textile effluents and in water re-use in terms of
  - initial cost,
  - simplicity of design,
  - ease of operation and
  - insensitivity to toxic substances (Meshko et al., 2001).
- Activated carbon is the most widely used adsorbent for adsorption process because it has a high capacity for the adsorption of organics, but its use is limited due to its high cost.

2

Contn'd

- This has led the researchers for cheaper and more effective substitutions for adsorbant materials.
- In this study, natural materials that are "basaltic tephra" and "clinoptilolite" were used to remove various dyestuffs from the wastewater of textile industry.
- Textile industry is one of the leading industries in Turkey.
- These materials are cheap and available in large quantities in Turkey.

3

MATERIAL AND METHODS

- **Adsorbents.** Basaltic tephra and clinoptilolite
  - Basaltic tephra is a kind of volcanic stone that is containing large amount of gas space formed by dissociation of evolved gases due to rapid cooling of magma.
  - Clinoptilolite is a natural zeolite mineral and is a natural Aluminum Silicate. Clinoptilolite, like most of the zeolites, has a three-dimensional crystal structure and it contains two-dimensional channels in it.

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MATERIALS (contn'd.)

Chemical composition of the basaltic tephra and clinoptilolite

Constituent	Basaltic tephra, % by weight	Clinoptilolite, % by weight
SiO_2	47.35	76.86
Al_2O_3	19.99	14.61
CaO	9.23	2.11
Fe_2O_3	12.26	1.24
MgO	4.03	0.76
Na_2O	2.97	0.65
K_2O	2.56	3.77
TiO_2	1.61	-

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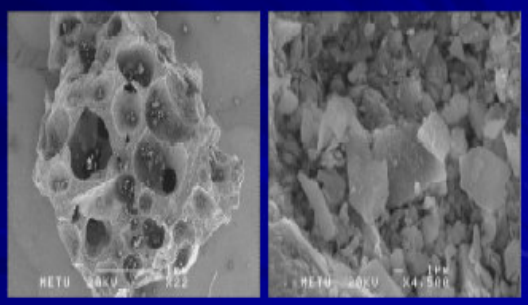
MATERIALS (cont.)

SEM photographs of the basaltic tephra



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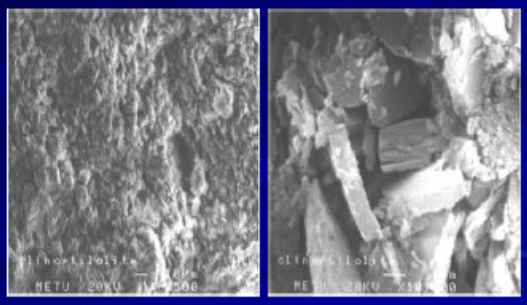
MATERIALS (contn'd)

SEM photographs of the clinoptilolite



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MATERIAL AND METHODS

Table 1. Dyestuffs used in the experiments

Commercial Name	Color Index	Chemical Class	Abbreviations
Setacryl Golden Yellow GL	Basic Yellow 28	Methine	BY
Setacryl Blue FGRL	Basic Blue Mix	Mix	BB
Nyloset Yellow SN6G	Acidic Yellow 95	Azo	AY
Nyloset Red EBL	Acidic Red 57	Monoazo	AR

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PHYSICAL PROPERTIES OF ADSORBENTS

- **Particle sizes**
  - basaltic tephra (d_p<0.60 mm and 0.60 mm <d_p<1.00 mm)
  - clinoptilolite (d_p<0.50 mm and d_p<0.063 mm)
- The **surface areas**
  - 6.4 and 4.2 m^2/g for basaltic tephra
  - 36.7 and 28.4 m^2/g for clinoptilolite

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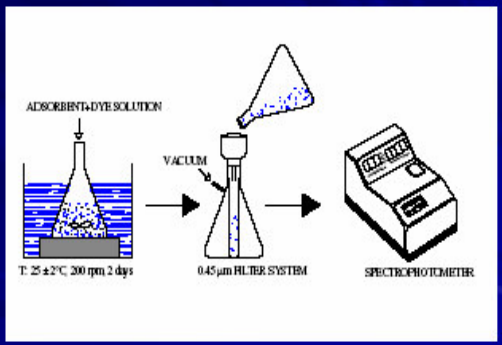
EXPERIMENTAL SETUP



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EXPERIMENTAL PROCEDURE

- A fixed amount of dry adsorbent (0.1 g) with 100 mL dye solutions at 8 different were shaken at 200 rpm and 25±2°C for 2 days.
- 20 mL of a sample was filtered through 0.45 µm filter system.
- Dye concentrations of the filtered solutions was measured by using the spectrophotometer with a 1 cm path length.

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Contn'd

- Adsorption isotherms were plotted to see the relationship between adsorption capacity of the adsorbent and equilibrium concentration of the adsorbate.
- It was noted during the filtration of solutions through 0.45 µm filter system that filter paper adsorbs the dye to a small extent for various dyes. The concentration measurements for all the adsorption experiments were corrected for this adsorption.

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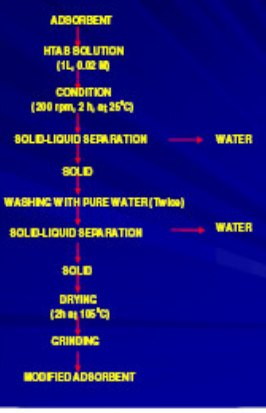
MODIFICATION OF SURFACE PROPERTIES



RESULTS AND DISCUSSION

- Effect of Particle Size on Adsorption
  - Higher adsorption capacity was obtained for the smaller particle size as expected.

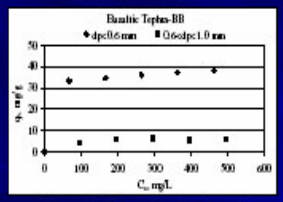


Figure 1. Adsorption isotherms for basic blue on two sizes of basaltic tephra

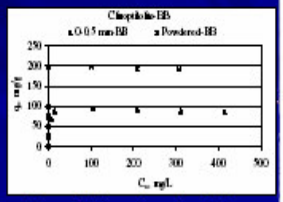


Figure 2. Adsorption of basic blue onto natural clinoptilolite

EFFECT OF SURFACE MODIFICATION ON ZETA POTENTIAL

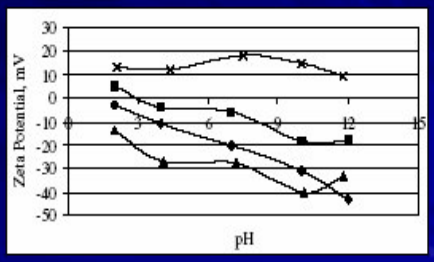


Figure 3. Zeta potential vs pH profiles of natural and modified adsorbents (◆ Natural Tephra, ■ Modified Tephra, ▲ Natural Clinoptilolite, x Modified Clinoptilolite)

EFFECT OF SURFACE MODIFICATION ON SURFACE AREAS

Table 2. Surface areas of the natural and modified adsorbents

Material	BET Surface Area, m^2/g
Basaltic Tephra, <0.60 mm	6.44
Modified Tephra	2.73
Clinoptilolite, <0.063 mm	36.65
Modified Clinoptilolite	19.14

EFFECT OF SURFACE MODIFICATION ON INCREMENTAL PORE AREA

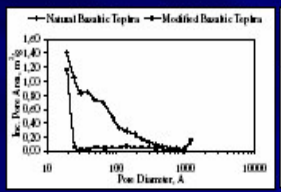


Figure 4. Incremental pore area versus pore diameter plot for basaltic tephra

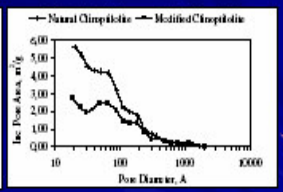


Figure 5. Incremental pore area versus pore diameter plot for clinoptilolite

EFFECT OF SURFACE MODIFICATION ON INCREMENTAL PORE VOLUME

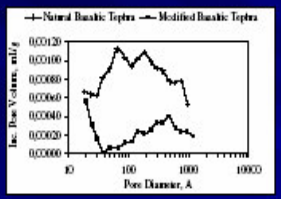


Figure 6. Incremental pore volume versus pore diameter plot for basaltic tephra

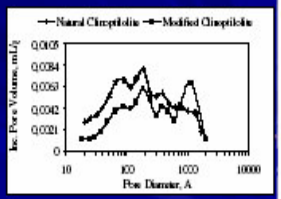


Figure 7. Incremental pore volume versus pore diameter plot for clinoptilolite

Table 3. Average pore diameter and total pore volumes of the natural and modified adsorbents

Material	Average Pore Diameter, A	Total Pore Volume, mL/g
Basaltic Tephra, 0-0.60 mm	92.6	0.0184
Modified Basaltic Tephra	62.6	0.0043
Clinoptilolite, Powdered Form	96.5	0.0884
Modified Clinoptilolite	132.4	0.0633

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q_e vs C_e Data

- Before modification,

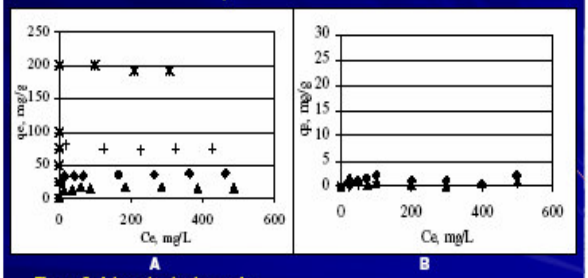

Figure 8. Adsorption isotherms for
A- basic dyes (♦Tephra-BB, ▲ Tephra-BY, ⁎ Clinoptilolite-BB, + Clinoptilolite-BY)
B- acidic dyes (♦Tephra-AY, ▲ Tephra-AR, ⁎ Clinoptilolite-AY, + Clinoptilolite-AR)

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q_e vs C_e Data

- After modification,

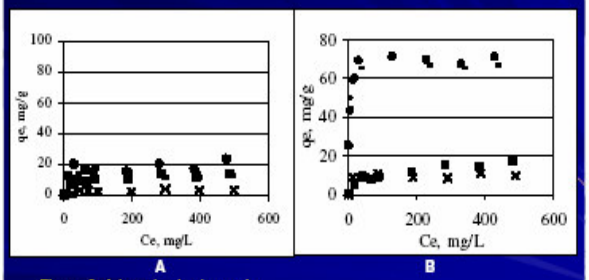

Figure 9. Adsorption isotherms for
A- basic dyes (■Tephra-BB, x Tephra-BY, ♦ Clinoptilolite-BB, - Clinoptilolite-BY)
B- acidic dyes (■Tephra-AY, x Tephra-AR, ♦ Clinoptilolite-AY, - Clinoptilolite-AR)

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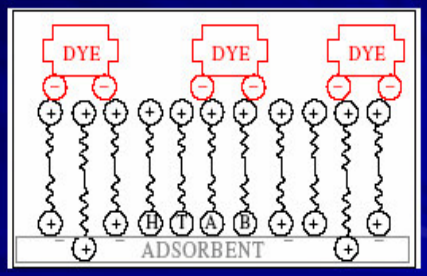
Schematic illustration of the interaction of dyes with modified adsorbents



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ADSORPTION ISOTHERMS

- Langmuir Isotherm Equation;

$$\theta = q_e / q_{mon} = K_L C_e / (1 + K_L C_e)$$
$$C_e / q_e = (1 / K_L q_{mon}) + (1 / q_{mon}) C_e$$

Where;

q_e = the amount of dyes adsorbed per unit mass of adsorbent

C_e = final concentrations of dyes in the aqueous phase

q_{mo} = the amount of dye adsorbed corresponding to monolayer coverage

K_L & q_{mon} can be found from the graph of (C_e/q_e) versus C_e

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ADSORPTION ISOTHERMS (cont.)

- *The Freundlich expression* is an exponential equation and therefore, assumes that as the adsorbate concentration increases so does the concentration of adsorbate on the adsorbent surface.
- Freundlich Isotherm equation;

$$q_e = K_F C_e^{bF}$$

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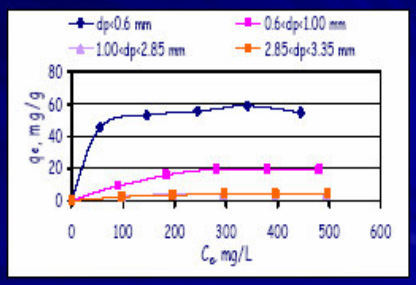
Adsorption isotherms for different sizes of basaltic tephra



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Adsorption isotherms for different sizes of clinoptilolite

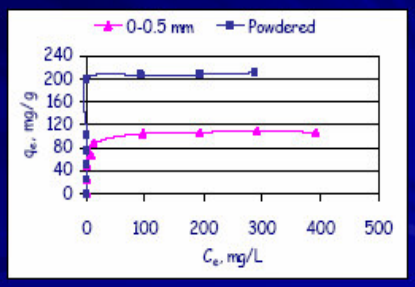

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Table 4. Langmuir isotherm constants for natural and modified adsorbents

Adsorbent	Dye	q_{max} (mg/g)	K_L (L/g)	R_L	R^2
Natural Tephra	BB	38.1	0.13	0.015	0.998
Modified Tephra	BB	13.6	0.04	0.045	0.992
Natural Tephra	BY	14.1	0.17	0.012	0.992
Modified Tephra	BY	3.8	0.02	0.106	0.934
Natural Clinoptilolite	BY	74.1	5.19	0.001	0.999
Modified Clinoptilolite	BY	11.9	0.09	0.023	0.985
Natural Clinoptilolite	BB	192.3	2.60	0.001	0.999
Modified Clinoptilolite	BB	21.3	0.04	0.050	0.943
Modified Tephra	AY	18.4	0.01	0.129	0.975
Modified Tephra	AR	9.7	0.23	0.009	0.980
Modified Clinoptilolite	AY	69.9	0.52	0.003	0.998
Modified Clinoptilolite	AR	66.2	1.31	0.001	0.999

Correlation coefficients for Langmuir Equation for natural and modified adsorbents give a very good fit with Langmuir Isotherm Equation.

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CONCLUSIONS

- Basaltic tephra and clinoptilolite in their natural forms can be used for the adsorption of basic dyes (cationic dyes). Clinoptilolite gives about 5 times better adsorption capacity than "basaltic tephra".
- The adsorption capacities of basaltic tephra and clinoptilolite in their natural form for the adsorption of acidic (anionic dyes) are not high enough.
- If surface modifications of these adsorbents are done with a surfactant, like HTAB, the adsorption capacities of basaltic tephra and clinoptilolite for anionic dyes are increased several times based on the type of the dye. Modified clinoptilolite 3-7 times has higher adsorption capacity for acidic dyes than modified basaltic tephra.
- Langmuir Isotherm Equation represents the adsorption of all dyestuffs on the adsorbents used in this study better than Freundlich Isotherm Equation.

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THERMODYNAMIC MODELING OF INORGANIC CHEMICAL SPECIES IN NATURAL POLLUTED WATERS

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Abstract

The natural waters are a vital source for human society. They are complex multicomponent systems containing major, minor and trace elements in different concentrations depending on the origin of the water basin. Nowadays, with the increasing urban and economic industrial and agricultural activities the pollution of water increases and poses a serious problem of human health and the environment. The major pollutants are nutrients and trace metals. During their transport in rivers they undergo numerous changes significant in zones of estuaries and sea. Monitoring investigations usually show the total content of the pollutants, without defining their chemical species, which determine the toxicity and bioavailability in the ecosystem.

Different inorganic metal species exist in natural waters depending on the medium composition, pH and redox potential. The metal-ligand interactions define the activities of the different complexes in the solutions. The different metal ions compete for coordination with the anions or with water molecules. The activity of each of the different complexes in the solution is influenced by the whole composition of the system. The different concentrations of analogous (HCO3-, SO42- and Cl-) anions in river and seawaters and the trend of Men+ to coordinate dominantly with some of them determine the differences of inorganic chemical species.

Thermodynamic modeling of the inorganic chemical species of the pollutants (nutrients and trace metals Fe, Mn, Zn, Cu, Cd and Pb) contents in waters of river - estuary – sea systems was has been achieved using a thermodynamic ion-association model (PHREEQCI computer program). The case studies were Kamchiya and Ropotamo rivers, a part of the Bulgarian Black Sea water catchment area, during the years 2004-2005.

The modelling data show the predominating forms of the nutrient chemical species in all river – estuary – sea water systems are free NO3- and NO2- ions, whose amount is practically the same as their total concentration. The dominant species of inorganic P in the river waters are H2PO4- and HPO42-. In sea waters the concentration of the former decreases by 1-2 orders of magnitude.

The trace metals Fe, Mn, Cu, Zn, Cd and Pb form a great variety of complexes, so different chemical species are typical of them in the systems studied.

Mn and Zn show analogous behaviour in the systems studied. The free Me2+ ions are predominating in all river-estuary-sea systems and their concentrations approach the total Mn and Zn concentration. The concentration of MeHCO3+, MeCO30 and MeSO40 is by 1-2 orders of magnitude lower than the Me2+ content in river waters. In sea water, due to the higher content of SO42- and Cl- ions, the concentration of MeHCO3+ decreases with one order of magnitude at the expense of MeSO40, Zn(SO4)22-, ZnOHCl0 and MeCln2-n (n=1÷4).

Cu and Pb also demonstrate analogous behaviour in the systems studied. Dominant Cu(+2) species in river water are CuCO30 (10-8 mol.kg-1 H2O) and Cu2+ (10-8 mol.kg-1 H2O), while the species CuCO30 and Cu(CO3)22- are dominating in estuary and sea waters. The concentration of CuOH+ (10-9 mol.kg-1 H2O) is a constant in both river and sea waters, but the concentration of the CuHCO3+ (10-9 mol.kg-1 H2O) decreases with one order of magnitude in sea water at the expense of CuOHCO3-. The species CuSO40 (10-10 mol.kg-1 H2O) reveal constancy in river and sea water, while the chloride complexes concentration increases significantly in sea water. Dominant lead species in river water are Pb2+, PbCO30 and PbHCO3+ ions (10-9 mol.kg-1 H2O), while PbCO30, PbCl+ and Pb(CO3)22- are prevailing in sea water. The concentrations of PbCln2-n (n=1-4), Pb(CO3)22- , PbOHCO3-, PbSO40 and Pb(SO4)22- complexes quickly increase in sea water.

Cadmium displays different behaviours in river and seawaters. In river and estuary waters free Cd2+ ions are prevalent and form the total Cd amount, whereas in sea waters CdCln2-n (n = 1–3) complexes prevail. The species CdSO4, CdCO3, CdHCO3+ form the second group of species in river waters which concentrations are in the range 10-13 -10-12 mol.kg-1 H2O. Completely different is a second group of species in sea water - Cd(SO4)34- CdSO40, CdOHCl0, CdCl42-, Cd(SO4)22-, CdCO30 and Cd(SO4)46-. Their concentrations vary in the range 10-11 -10-10 mol.kg-1 H2O.

The hydroxy forms Fe(OH)2+, Fe(OH)2+, Fe(OH)30 and Fe(OH)4- are species typical of Fe3+. Dominant species are Fe(OH)2+ in all river – estuary – sea water systems and their amount (10-5 - 10-6 mol.kg-1H2O) approaches to the total Fe concentration. Next in amount are the Fe(OH)30 species, whose concentration in river water is by 1-2 orders of magnitude smaller, but quickly increases with the solution pH and in sea water becomes comparable to Fe(OH)2+ species.

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THERMODYNAMIC MODELING OF INORGANIC CHEMICAL SPECIES IN NATURAL POLLUTED WATERS

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May 7-12, 2006, Istanbul, TURKEY

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WATER AS A MULTICOMPONENT SYSTEM:

- major, minor, trace elements

WATER MAJOR POLLUTANTS

- nutrients;
- trace metals.

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MONITORING PROBLEM

- It usually shows the total content of the pollutants, without defining their chemical species, which determine the toxicity and bioavailability in the ecosystem.

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AIM

- Determination of the inorganic chemical species in natural waters by:
  - chemical analyses; and
  - thermodynamic modeling of the systems.

CASE STUDIES:

- Water system *river - estuary – sea*

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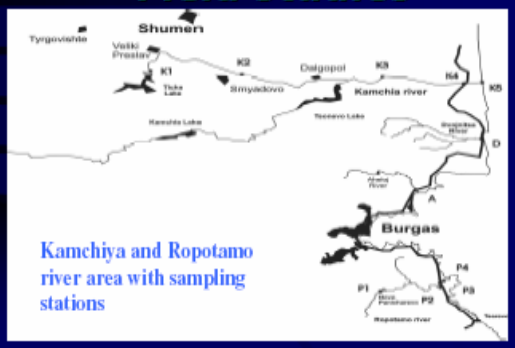
Field studies



Kamchiya and Ropotamo river area with sampling stations

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Chemical Analysis

- Nutrients (NO_3^- NO_2^-, PO_4^{3-}) Spectrophotometrically
- Dissolved Fe, Mn, Pb, Cd, Cu and Zn

Atomic Absorption Spectrometry(GFAAS)

- Dissolved oxygen

Vinkler procedure

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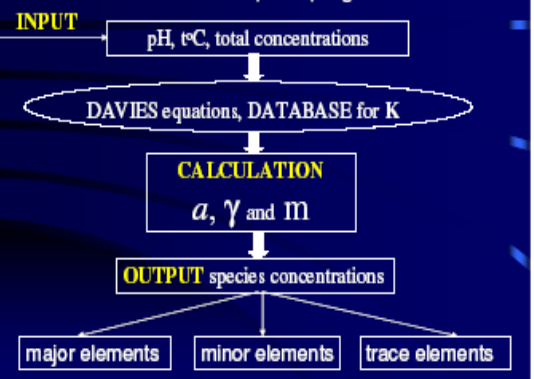
Thermodynamic Ion-Association Model

- The model uses extensions of the Debye-Huckel theory.
- The formation of each aqueous complex is defined by a mass-action expression with the appropriate association constant.
- The program claims calculation of the activity coefficients of the species that are valid up to an ionic strength approximately 0.7 mol.kg-1H2O.

Thermodynamic modelling

PHREEQCI computer program



KNOWN THERMODYNAMIC DATABASES:

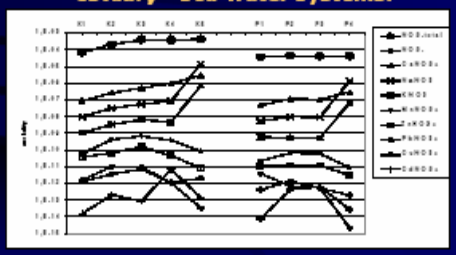
- They do not include data on the possible metal phosphate and nitrite complexes;

NEW THERMODYNAMIC DATABASE:

- Includes 61 more complexes (phosphates, nitrites, hydroxides, carbonates, sulfates, nitrates and chlorides).

RESULTS

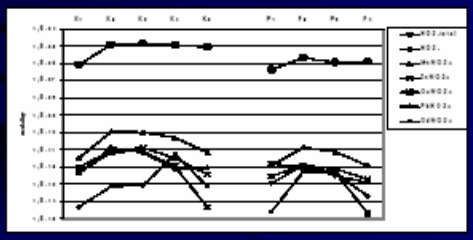
Speciation distribution of the NO3- in the *river – estuary - sea* water systems.



Dominant species – free NO3-

RESULTS

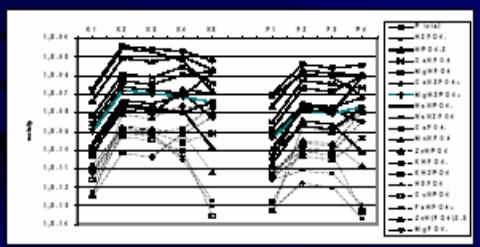
Speciation distribution of the NO2-in the *river – estuary - sea* water systems.



Dominant species – free NO2-

RESULTS

Speciation distribution of the P in the *river – estuary - sea* water systems.



Dominant species – free H2PO4- and HPO42-

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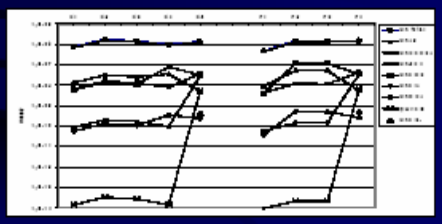
RESULTS

Speciation distribution of the Mn(+2) in the *river – estuary - sea* water systems.



Dominant species – free Mn(+2)

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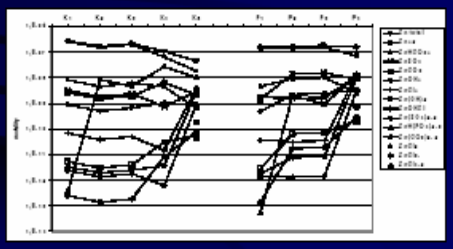
RESULTS

Speciation distribution of the Zn(+2) in the *river – estuary - sea* water systems.



Dominant species – free Zn(+2)

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RESULTS

Speciation distribution of the Cu (+2) in the *river – estuary - sea* water systems.

Dominant species: river – CuCO3 0 and Cu2+ ;

Estuary and Sea - CuCO3 0 and Cu(CO3)2 2-

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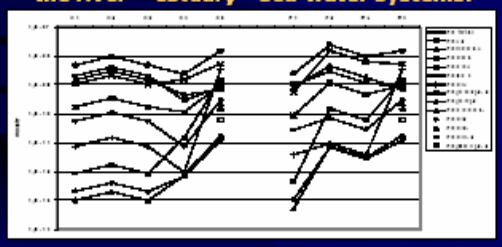
RESULTS

Speciation distribution of the Pb (+2) in the *river – estuary - sea* water systems.



Dominant species: river – PbCO3 0, PbHCO3+, Pb2+
Sea -PbCO30, PbCl+ and Pb(CO3)22

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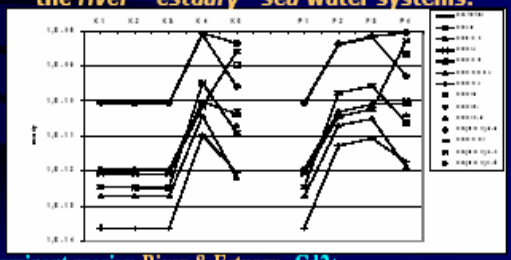
RESULTS

Speciation distribution of the Cd (+2) in the *river – estuary - sea* water systems.



Dominant species: River & Estuary –Cd2+
Sea -CdCln2-n (n = 1–3)

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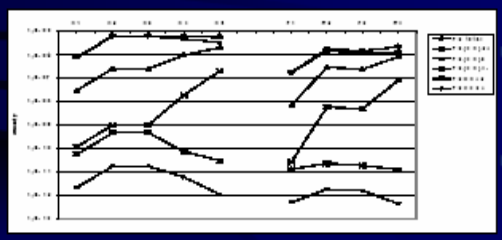
RESULTS

Speciation distribution of the Fe(+3) in the *river – estuary - sea* water systems.



Dominant species - Fe(OH)2+

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Thank You for the Attention
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THE NATIONAL CLEANER PRODUCTION PROGRAMME BENEFITS ASSESSMENT

Ales Komar[1], **Frantisek Bozek**[2], **Jiri Dvorak**[3]

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1 Report on the Assessed Time Period

Four **special manuals** (in both software and printed versions) have been developed within the scientific and research project called – „**Technical Manual for the Prevention and Minimization of Waste**“. They include preventive measures for the **textile and paper industries, car wreckage disposal, disposal of electric and electronic installations and treatment of metal surfaces**. The technical manuals supplement a **general manual** aimed at **waste minimization**. The special manuals have been tested in real operations and in IPPC processes.

Project co-operation continued with UNIDO and UNEP, which cover cleaner production (CP) on an international level.

Since September 1st, 2004 the agenda of the **National Cleaner Production Agency** has been delegated to the **Czech Environmental Information Agency (CENIA)** on the basis of an MoE Decree and with agreement of the management board of the Czech Centre of Cleaner Production. The Czech Centre of Cleaner Production was renamed the **Centre of Innovations and Development** on the 1st of January 2005.

Promotion of cleaner production has been strengthened recently. **Web pages** have been designed in order to promote cleaner production and to disseminate theoretical knowledge and practical experience acquired in the field of cleaner production.

A project proposal has been developed together with a manual focused on the implementation of **cleaner production in medical facilities** under Vysočina district control. The project „**Cleaner Company**“ is in its first phase.

An **annual report** on the handling of tasks within the National Cleaner Production Programme will be part of a **Report on the Environment**. It will be elaborated by the National Programme Agency which will ensure the outcomes of National Cleaner Production Programme will be archived and published on the internet (Czech Government Decree No 152/2006).

2 Balance of the Decade of Implementing Cleaner Production in the Czech Republic

Cleaner production projects have been **implemented in 91 companies**. The companies operate in the fields of light and heavy industries, the chemical, textile and food industries, medical service, the production of costume jewellery, agriculture, bakeries, breweries and forestry.

Besides the above mentioned projects the Cleaner Production Centre arranged grants from the State Environment Fund within the programme supporting cleaner production, which was later transferred to the **support of best available technologies**. Projects were also focused on introducing HACCP in food industry economic entities.

From 1992 to 2004 there were **118 projects implemented**, 32% of which achieved financial savings. In the year following the implementation of cleaner production **37 companies saved 7,2 million USD** altogether (this figure represents 32% out of 118 projects). The average amount of savings reached almost 0,2 million USD. The **payback period** varied from 0 to 72 months, **27 months at average**, and Internal Rate of Return (IRR) was around 17 %.

3 Current Topics

The following activities are being prepared within the National Cleaner Production Programme for the period of 2005-2006:

a) Promotion strengthened through **web pages** managed by CENIA and the continuous updating of their content (current news, info on the projects);

b) Realization of the **cleaner production project in medical facilities** and the finish of „Cleaner Company“ **project**;

c) Retention of financial support from the State Environment Fund – **BAT Programme for the cleaner production projects**;

d) Participation of the Czech Republic in the **PREPARE network** (**Preventive Environmental Protection Approaches in Europe**) under the auspices of EUREKA international network and in co-operation with EuroEnviron environmental agency;

e) Broader participation of companies in the decision-making process about the National Cleaner Production Programme (**reconstruction of the Board of National Cleaner Production Programme**).

UTILIZATION OF CLEANER PRODUCTION AND THE BEST AVAILABLE TECHNOLOGY IN A FOOD PROCESSING PLANT

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Abstract

At present prime attention is paid to minimizing and utilizing of biodegradable waste as a significant type of waste. Pastry production is a typical example, because it processes raw materials which are subject to rapid degradation as well as products which are valueless once they lose their freshness.

Non-consumed pastry is commonly utilized in agriculture as feed. Utilization in large-scale breeding is problematic, though. Effective breeding of livestock is based on prepared, optimum fodder rations. The addition of non-consumed pastry is not considered in such cases. That is why it is necessary to seek out the possibility of use of non-consumed pastry by private farmers and small breeders. Regular demand is not guaranteed by these target groups. In case of bad estimate of demand for pastry a larger amount of non-consumed pastry and bakery products remain to be disposed of.

Economic and environmental benefits resulting from the implementation of cleaner production methodology and bat in food industry have been clearly proved on the example of a bakery. It has been based on the substitution of an obsolete yeast production technology with the best available technology (bat) enabling production of durable, high-quality yeast as well as utilization of non-consumed pastry which has not been sold elsewhere due to bad estimate of demand. Up to 20% of flour as the original raw material can be substituted for pastry from the previous day production which has not been sold. That pastry was previously disposed in a waste incineration plant.

UTILIZATION OF CLEANER PRODUCTION AND THE BEST AVAILABLE TECHNOLOGY IN A FOOD PROCESSING PLANT

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INTRODUCTION

At present prime attention is paid to minimizing and utilizing of biodegradable waste as a significant type of waste. Pastry production is a typical example, because it processes raw materials which are subject to rapid degradation as well as products which are valueless once they lose their freshness.

Non-consumed pastry is commonly utilized in agriculture as feed. Utilization in large-scale breeding is problematic, though. Effective breeding of livestock is based on prepared, optimum fodder rations. The addition of non-consumed pastry is not considered in such cases. That is why it is necessary to seek out the possibility of use of non-consumed pastry by private farmers and small breeders. Regular demand is not guaranteed by these target groups. In case of bad estimate of demand for pastry a larger amount of non-consumed pastry and bakery products remain to be disposed of.

PROCESS ANALYSIS

Internal recycling can be an effective solution to the problem of non-consumed pastry besides typical measures of cleaner production. Possibility to implement internal recycling has been verified in the HEPEK, Ltd. bakery in Brno, Zabrdovice.

Originally 112 $t.year^{-1}$ of produced pastry remained non-consumed out, of which 77 $t.year^{-1}$ were used as feed. The remaining amount of 35 $t.year^{-1}$ was incinerated in the Brno municipal waste incineration plant. The company has met the legal regulation. However, the bakery management considered this way of disposing stale pastry to be inefficient. The incineration has not been reasonable from the economic viewpoint either, because the price for the incineration ran into 45 $USD.t^{-1}$ of waste.

Zabrdovice bread

Zabrdovice rolls

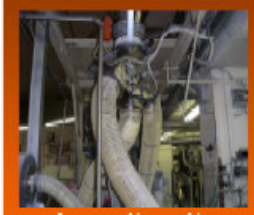
CHARACTERISTICS OF PASTRY PRODUCTION PROCESS

During mechanized production dough is produced continually from wheat and rye flour with addition of durable rye leavens, solutions of salt and yeast, caraway and drinking water in a masticator. Dough goes to a graduation machine through a conveyer. Required weight of dough is separated and formed into a shape of bread roll on a rolling machine.

Stiring of leaven

The semi-product is put into a scuttle with a special device. The scuttle has got a fabric lining and is in a tray-type proofer. After proofing, bread is automatically removed onto a metal baking belt of a continuous oven heated by natural gas. Baked bread is cooled by nozzles with drinking water.

OBJECTIVES OF PROJECT


Leaven making machine for making clear fermentation culture

The BAT for the production of durable leavens has been installed in the company. In contrast to other dough leaven processes cca 20 % of dough can be substituted for non-dispatched wheat-rye bread, which has got extremely positive effects on fermentation. Due to longer fermentation time and high water content there is wheat-rye bread and wheat pastry of high quality, longer durability and bigger volume with the savings of additives, especially yeast, fat and sugar. At the same time the product has got more distinctive taste and aroma.

The proposed line consists of the following complex of equipment

a) leavenmaking machine equipped with a proportioning pump as well as a device for crushing pastry and weighing on tenzometers;
b) leavenmaking machine for making clear fermentation culture
c) ripening tanks with the stirring of leaven;
d) leaven distribution systems from leavenmaking machines to ripening tanks and from the ripening tanks to masticators;
e) transport of flour and leaven into fermentation machines
f) water dosers adding water into fermentation machines and a masticator;
g) control system and its check.

Production of final leaven is carried out in the machinery which has a hard bread self-crushing device.

Fermentation machine

Durability of leaven, guaranteed by a producer to be up to 7 days, is important for the optimum course of leaven preparation process. Preparation of leaven with a durability of approx. 0,5 hour had been carried out before the above mentioned technology was implemented. After this time period lactic fermentation changed to alcohol fermentation and if the process was not stopped by adding flour the whole batch could not be used any more and the whole process had to be repeated.

ECONOMIC AND ENVIRONMENTAL BENEFITS

Total investment in the new technology was approximately 1,3 10^5 USD. Economic and environmental benefits achieved after implementing BAT are evident from the following charts No 1-4.

Chart No 1 Production process expenses

Type of expense	Primary expenses [USD year⁻¹]	Current expenses [USD year⁻¹]	Difference [USD year⁻¹]
Raw materials costs	990 572	987 389	9 983
Secondary and subsidiary materials costs	-	-	-
Power and fuel expenses	68 080	63 619	4 461
Raw materials transport costs	-	-	-
Labour costs	194 546	185 849	8 697
Maintenance costs	-	-	-
Other operating expenses	-	-	-
Total	1 050 198	1 037 257	12 941

Chart No 2 Waste expenses

Type of expenses	Primary expenses [USD year⁻¹]	Current expenses [USD year⁻¹]	Difference [USD year⁻¹]
Waste collection, separation and storage costs	2 900	2 900	0,0
Waste transport costs	-	-	-
Waste disposal costs	1 575	0,0	1 575
Terminal technologies operating costs	-	-	-
Other expenses	-	-	-
Total	4 475	2 900	1 575

Chart No 3 Environmental pollution charges

Charge factors	Primary amount [year⁻¹]	Current amount [year⁻¹]	Primary charges [USD year⁻¹]	Current charges [USD year⁻¹]	Difference [USD year⁻¹]
Household waste	-	-	-	-	-
Other waste	-	-	-	-	-
Hazardous waste	-	-	-	-	-
Water	-	-	-	-	-
Air	-	-	-	-	-
Soil	-	-	-	-	-
Power	217,478 GJ	208,228 GJ	3 545	3 313	232
Total			3 545	3 313	232

Chart No 4 Total savings and environmental benefits after the implementing measures

Types of savings	Amount of savings
Total investment	130 435 USD
Process savings	22 941 USD year⁻¹
Wastes savings	1 575 USD year⁻¹
Total savings	24 516 USD year⁻¹
The proportion of annual savings to total amount of investment	1,88 10^{-1} year⁻¹
Pollution charges savings	232 USD year⁻¹
The proportion of annual pollution charges savings to total amount of investment	1,78 10^{-3} year⁻¹

STATIC METHOD

Generation and allocation of company profit after the mentioned investment is shown in chart No 5. It holds for such a situation when depreciation of machines from investment costs is 6,2 % in the first year and 13,4 % in the following years. Profit tax is calculated to be 30 % and interests charged on loans are 7 %.

Chart No 5 Generation and allocation of profit after the implementing of measures

Year of payments	1	2	3	4	5
Revenues [USD]	70 438	70 438	70 438	70 438	70 438
Depreciation of machines [USD]	8 087	17 478	17 478	17 478	17 478
Interest [USD]	9 130	6 848	4 565	2 283	-
Gross profit [USD]	53 221	46 112	48 395	50 677	52 960
Profit tax [USD]	15 966	13 834	14 519	15 203	15 888
Profit after taxation [USD]	37 255	32 278	33 876	35 474	37 072
Depreciation of machines [USD]	8 087	17 478	17 478	17 478	17 478
Back-payment [USD]	32 609	32 609	32 609	32 608	-
Company profit [USD]	12 733	17 147	18 745	20 344	54 550

Payback period of investment PP is 2,4 years and it can be calculated according to the formula (1), where IN is the amount of investment and $CF_{(t)}$ is the cash flow of revenues in the year when the investment is paid back.

$$PP = \frac{IN}{CF_{(t)}} = \frac{130435}{54550} = 2{,}39 \text{ years} \qquad (1)$$

Present worth of investment in t year, $PW_{(t)}$ when loan rate $i = 0{,}07$ and the assumed payments equals $3{,}2.10^4$ USD year⁻¹, is $PW_{(t)} = 10^5$ USD at the time the investment is paid back as seen in equation (2).

$$PW_{(t)} = \frac{IN}{(1+i)^{-t}} = \frac{130435}{(1+0{,}07)^{-t}} = 99508 \text{ USD} \qquad (2)$$

DYNAMIC METHOD

When using a dynamic method of present value and internal discount rate K_i = 0,08 it can be found out that the mentioned investment will be profitable in the 4th year of operation and the profit will amount to $3{,}4.10^4$ USD. Total revenue of the investment during its service life, which is 8 years, exceeds the amount of $1{,}66.10^5$ USD. Calculation was made according to the formula (3) and (4), where $PVNB_{(t)}$ is a cumulated present net value in *t* year, $PVCF_{(t)}$ means cumulated present value of cash flow in t year, K_i is a internal discount rate, $CF_{(t)}$ is cash flow from a particular investment in *t* year and IN is the amount of investment

$$PVCF_{(t)} = \sum_{t=1}^{t} \frac{CF(t)}{(1+K_i)} \qquad (3)$$

$$PVNB_{(t)} = PVCF_{(t)} - IN \qquad (4)$$

The amount of $PVNB_{(t)}$ cumulated present net value of benefits of the investment in individual years as well as other necessary data are shown in Chart No 6.

Chart No 6 Cumulated present value of net benefits of investment in individual years

Year	Investment costs [USD]	Company $CF_{(t)}$ [USD]	$(1+K_i)^t$	Present value of $CF_{(t)}$ [USD]	Cumulated present net value of benefits $PVNB_{(t)}$ [USD]
0	130 435	-	1,000	- 130 435	- 130 435
1	-	45 362	1,080	41 983	- 88 452
2	-	49 793	1,166	42 655	- 45 797
3	-	51 354	1,260	40 756	- 5 041
4	-	52 952	1,360	38 931	+ 33 890
5	-	54 550	1,469	37 126	+ 71 016
6	-	54 550	1,587	34 378	+ 105 392
7	-	54 550	1,714	31 829	+ 137 221
8	-	54 550	1,851	29 472	+ 166 693

INTERNAL RATE OF RETURN

Under the assumption that the service life of investment is 8 years the IRR was calculated with the help of formula (5) to be 35 %. As the analytic solution of equation is difficult the approximation method was used in compliance with formula (6), where S_1 is a cumulated present value of cash flow in a year of investment service life, i_1 is an appraised interest rate for which $S_1 > 0$; S_2 is an analogical value of cash flow, i_2 is an interest rate for which $S_2 < 0$, and it holds that $i_2 > i_1$ and sums of S_1 and S_2 are sufficiently close to zero.

$$\sum_{t=1}^{t} \frac{CF_{(t)}}{(1+i)} = 0 \qquad (5)$$

$$IRR = 100 \cdot \{ i_1 + [S_1 \cdot (S_1 - S_2)^{-1}] \cdot (i_2 - i_1) \} \qquad (6)$$

CONCLUSION

Economic and environmental benefits resulting from the implementation of cleaner production methodology and BAT in food industry have been clearly proved on the example of a bakery. It has been based on the substitution of an obsolete leaven production technology by the BAT enabling production of durable, high-quality leaven as well as utilization of non-consumed pastry which has not been sold elsewhere due to bad estimate of demand.

Mixing machine

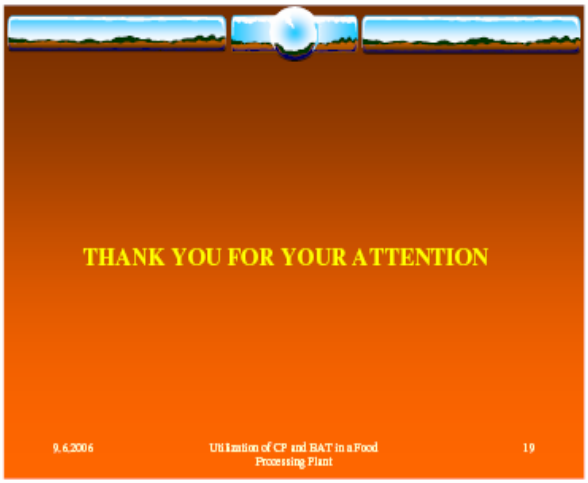
The implementation of technology required investment costs amounting to 1,3.105 USD and resulted in positive economic and environmental benefits not only for the company itself, but also for the society.

CONCLUSION

Based on the company performance before the implementation of technology the payback period of the investment has been assessed to be circa 2 years and 3 moths in case a static method was applied and roughly 3 years in case a dynamic method was applied. Company annual profit is approximately $2{,}5.10^4$ USD. The internal rate of return is 35 % under the assumption that the service life of installed machinery is 8 years. Company total profit from the sale of pastry in the first year after the measures were introduced was $2{,}6.10^5$ USD as compared with the calculated profit of $2{,}3.10^5$ USD and it corresponds with the above mentioned assumptions.

CONCLUSION

The environmental benefits were also achieved by the implementation of the measures. They are represented mainly by the substitution of non-consumed pastry for flour with in the production process and a significant reduction of energy consumption. The reduced energy consumption will result in the reduced environmental burden caused by emissions, which is, in economic indicators, approximately 232 USD of social savings each year.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Utilization of CP and BAT in a Food Processing Plant
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ENFORCEMENT OF ENVIRONMENTAL REGULATIONS IN ISRAEL - 2005

Chaim Forgacs

The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva, Israel (forgacs@bgumail.bgu.ac.il)

Abstract

The last year brought substantial changes in the approach of the authorities (national and municipal) to the enforcement of environmental regulations. While in the past fear from raising unemployment resulted in a lenient attitude, recently more and more industrial entities are severely fined or even closed down because of unacceptable levels of pollution, or other environmental violations.

A major power station was shut down, for not switching in time to natural gas. Chemical plants in the Haifa bay and in the Ramat Chovav Industrial Park were reprimanded, fined and their operations temporarily restricted.

A few of these cases will be discussed in detail.

Enforcement of Environmental Regulations in Israel - 2005

Chaim Forgacs
Israel

Abstract

- The last year brought substantial changes in the approach of the authorities (national and municipal) to the enforcement of environmental regulations. While in the past fear from raising unemployment resulted in a lenient attitude, recently more and more industrial entities are severely fined or even closed down because of unacceptable levels of pollution, or other environmental violations.
- A major power station was shut down, for not switching in time to natural gas.
- Chemical plants in the Haifa bay and in the Ramat Chovav Industrial Park were reprimanded, fined and and their operations temporarily restricted.

Air pollution near the Tel Aviv power station

An in-house team of environmental specialists acts as our "watch-dog" – constantly ensuring that our own self-imposed, high environmental standards are fulfilled.

Since our customers justifiably demand high-performance products that do not compromise
the environment, HAIFA invests millions of dollars annually in eliminating hazards, in
purification, and recycling effluents into viable products.
These extensive efforts have assured the development of market-leading,
environmental-friendly products.

Haifa's production processes meet the requirements of the ISO-14000 standard.

The Krayot Magistrates Court fined Haifa Chemicals a total of NIS 584,000 (about $125,000) for offenses under the Prevention of Sea Pollution from Land-Based Sources Law. According to the indictment, Haifa Chemicals and one of its senior officials did not comply with conditions specified in their discharge permit in relation to reporting and planning requirements. In addition, the defendants were accused of discharging wastewater to the sea via the Kishon River during the years 2001 and 2002 at quantities which exceeded permitted values for different materials under the permit.

In the past, Haifa Chemicals was one of the major polluters of both the Kishon River and the Mediterranean Sea. High acidity, heavy metals and high nitrogen and phosphorus loads precluded the possibility of any life in the river. However, in recent years major improvements in effluent quality levels from Haifa Chemicals have been achieved in accordance to discharge permits.These improvements are largely attributed to enforcement efforts by the Environment Ministry.

As part of a plea bargain agreement between the Environment Ministry and Haifa Chemicals, the factory was convicted of offenses under the Prevention of Sea Pollution from Land-Based Sources Law while charges against the official were dropped. On November 29, 2005, the court imposed a fine of NIS 584,000 on the company, a fine higher than that agreed upon in the plea bargain.

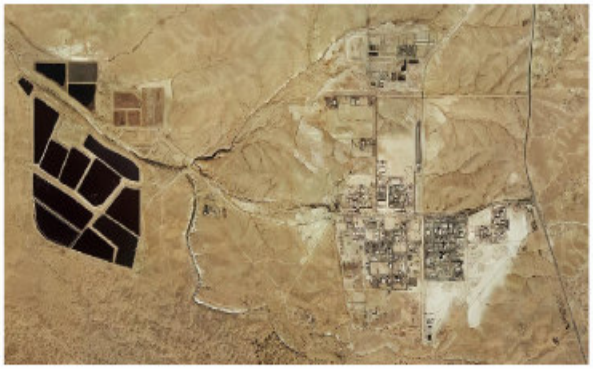
On January 11, 2006, the Haifa Magistrates Court imposed an unprecedented fine - NIS 1.6 million - on Oil Refineries Ltd. for air pollution offenses under the Abatement of Nuisances Law. The fine, the highest ever to be levied under this law, is also the maximum possible fine for this type of offense.

The company was fined for causing air pollution in the Haifa Bay area on two occasions in 2003: September 15, 2003 and October 5, 2003 (the Eve of Yom Kippur). Air pollution emissions were triggered by problems in the operational systems of the plant and in the gas combustion system. The result: a dark, heavy and thick cloud rose high up from the torches of the oil refineries for a three hour period (and five hours on Yom Kippur Eve) and covered the Haifa Bay area. During the entire time that the black smoke was emitted from the oil refineries, residents were asked to remain in their homes so as to minimize exposure to air pollution.

Oil Refineries Ltd is the only company in Israel that refines crude oil and supplies petroleum products. Its Haifa and Ashdod refineries have a combined refining capacity of 13 million tons of crude oil per year.

The Ministry of the Environment is responsible for Israel's National Monitoring Program for the Mediterranean Sea, which is carried out by Israel Oceanographic and Limnological Research under the professional guidance of the ministry's Marine and Coastal Environment Division. The overall objective of the program is to provide a scientific basis for decision making with regard to protection of the coastal environment, including enforcement of relevant national legislation and international conventions. The program includes the following components:

* Monitoring of heavy metals in coastal waters (carried out since 1978);
* Monitoring of the introduction of nutrients and particulate metals into coastal waters through coastal rivers (since 1990);
* Monitoring of atmospheric fluxes of nutrients and heavy metals into coastal waters (since 1996);
* Monitoring of nutrient levels and algal populations in the shallow area of the coastal waters (since 2000);
* Microbial pollution in bathing beaches (conducted by the Ministry of Health).



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URBAN WATER SERVICES DEVELOPMENT - ROMANIAN PERSPECTIVE

Viorel Harceag

National Company for Investments, Bucharest, Romania
(viorelh@vio.cbi.ro)

Abstract

In general, Romania's environmental infrastructure does not comply with the EU directives. It is also inefficient and subject to frequent breakdowns. In most cases, to fill in the approximation gap, Romania will have to build new infrastructure.

Out of Romania's 1,398 treatment plants, 601 produce drinking water for 11.3 million urban (cities with population> 5,000) dwellers (91%) and 797 for 3.4 million people in rural (localities with population < 5,000) areas (33%). The overall connection rate is 65%. Romania's 263 urban municipalities and 2,648 of Romania's 15,779 rural settlements (17%) have centralized water supply systems. Ten percent of the systems supplying water to the urban population do not comply with the limit values; this percentage goes up to 25% in rural areas.

Breakdowns are frequent in the water supply systems which are often up to 100 years old and in a bad state of repair. Supply is interrupted for more than 8hrs/day in 21% of urban agglomerations. The supply system and the distribution network are mostly made up of inadequate materials (asbestos-cement and lead, 30% of pipes are made of iron with no cleaning system). 70-75% of the existing system will have to be replaced. Drinking water is further contaminated with corrosion products and impurities resulting from frequent accidents. The intermittent supply also affects water quality. Domestic distribution systems that contain lead producing compounds will have to be changed.

Of the 3 billion m^3/year of wastewater requiring treatment, only about 20% is treated adequately, 30% inadequately, and 50% not treated at all, which means that about 80% of the wastewater discharged is insufficiently or not treated. 77% of households connected to the water supply have sewerage facilities; the overall connection rates are 91% for urban and 33% for rural. 47 out of 263 towns have either no treatment plants or plants that are not working properly; and of 15,779 rural settlements, only 53 have treatment facilities. Finally, more than half (58 percent) of the 1,441 wastewater treatment plants inventoried in 2000 were not working properly.

The PHARE study "Technical Assistance for the Elaboration of the Environmental Cost Assessment and Investment Plan" presumed that for Romania in a total cost of 39,034 MEURO to comply with environmental EU Directives, the estimated costs to comply with water related EU Directives will be 4,430 MEURO for potable water, 9,449 MEURO for urban wastewater treatment and 3,143 MEURO for nitrates (total for water sector = 17,022 MEURO).

Paper presents the potential financial sources for investments and prioritisation criteria for different projects. Financial sources for these investments could be: Internal (Government Budget, other domestic financial resources), EC Funding (Grants, Loans), International Financial Institutions (Loans), and International Donor Institutions (Grants). Prioritisation criteria have to include accession, environmental, financial, economic, technical, social and political, commercial and institutional criteria, taking into account affected population, pollution category of receiving water, number and complexity of project components, impact on protected and sensitive areas, size of investment, existence of a single operator, etc.

URBAN WATER SERVICES DEVELOPMENT - ROMANIAN PERSPECTIVE

Viorel Hârceag

NATO/ CCMS Pilot Study "CLEANER PRODUCTS AND PROCESSES"
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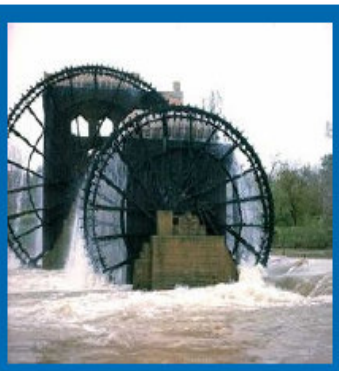

The Orontes River. Water wheels in Hama (Syria)

Water is the driving force of all nature

Leonardo da Vinci

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ESTIMATED COSTS TO COMPLY WITH WATER RELATED EU DIRECTIVES

Evaluated costs:

- Potable water 98/88/EEC: 4,430 MEURO;
- Urban WW Treatment 91/271/EEC: 9,449 MEURO;
- Nitrates 91/676/EEC: 3,143 MEURO;
- TOTAL -WATER SECTOR: 17,022 MEURO.
- TOTAL -all Directives: 39,034 MEURO

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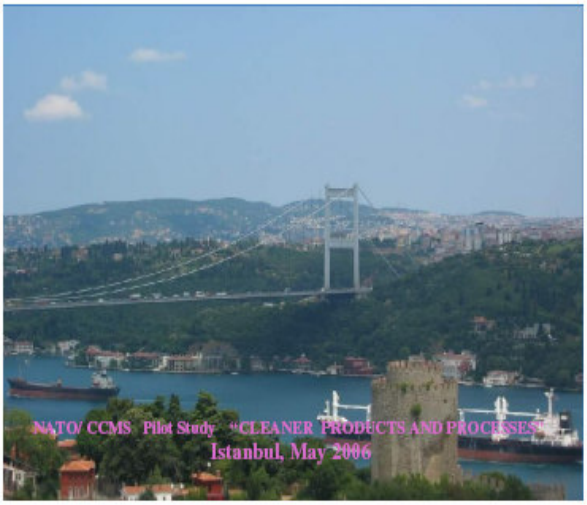

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Current situation

DRINKING WATER

(Localities with population > 5,000)

TOTAL NUMBER: 1,398 D.W. Treatment Plants

- ✓ 601 produce drinking water for 11.3 million urban dwellers (91% connection rate)
- ✓797 for 3.4 million people in rural areas (33%)

The overall connection rate is 65%

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Istanbul, May 2006

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Current situation

DRINKING WATER

- 263 urban municipalities and 2,648 of 15,779 rural settlements (17%) have centralized water supply systems
- Ten percent of the systems supplying water to the urban population do not comply with the limit values; this percentage goes up to 25% in rural areas

Current situation

DRINKING WATER

- Frequent breakdowns - water supply systems often up to 100 years old.
- Supply is interrupted for more than 8hrs/day in 21% of urban agglomerations.
- The supply system and the distribution network - mostly made up of inadequate materials (asbestos-cement and lead, 30% of pipes are made of iron with no cleaning system).

Current situation

DRINKING WATER

- Existing system - 70-75% have to be replaced.
- Drinking water is further contaminated with corrosion products and impurities resulting from frequent accidents.
- The intermittent supply also affects water quality.
- Domestic distribution systems that contain lead producing compounds have to be changed.

Current situation

WASTEWATER

- 3 billion m^3/year wastewater requiring treatment:
  - 20% - treated adequately
  - 30% - inadequately
  - 50% - not treated at all

80% of the discharged wastewater is insufficiently or not treated

Current situation

WASTEWATER

- 77% of households connected to the water supply have sewerage facilities
- The overall sewerage connection rates are 91% for urban and 33% for rural areas

Current situation

WASTEWATER

- 47 out of 263 towns have either no treatment plants or plants that are not working properly
- 53 of 15,779 rural settlements have treatment facilities.
- More than half (58 percent) of the 1,441 wastewater treatment plants inventoried in 2000 were not working properly.

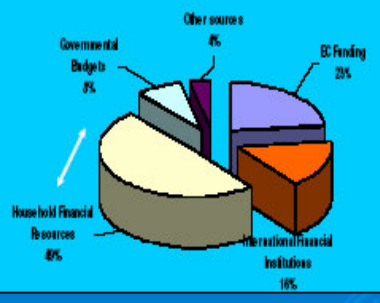
INVESTMENTS

TOTAL - WATER SECTOR: 17,022 MEURO

Financial sources:

- Internal (Government Budget, Other Domestic Financial Resources): direct investments
- EC Funding (Grants, Loans): ISPA, PHARE, Cohesion fund
- International Financial Institutions (Loans)
- International Donor Institutions (Grants)

Proposed structure of potential financing sources for environmental investments in 2006



PROJECTS PRIORITISATION CRITERIA

- Accession
- Environmental
- Financial
- Economic
- Technical
- Social & Political
- Commercial & Institutional

ACCESSION CRITERIA FOR PROJECT PRIORITISATION

Criterion	Comment/Description
Directive Priority	The priority allocated to a specific directive or sector in the context of the accession process
Directive transposition plans	The agreed transposition process and implementation plan of the directive (s) in question
Negotiated Implementation Position	The fulfilling of the negotiated position of the country with respect to this directive (for example, in relation to the agreed transition period)
Wider Implication	The wider implication of the project in the context of accession and future evolving EC environmental directives framework (for example, the emergence of the importance CO_2 reduction under the Kyoto protocol)

ENVIRONMENTAL CRITERIA FOR PROJECT PRIORITISATION

Criterion	*Comment/Description*
Environmental Benefits	The direct environmental benefits of a project (the scale & severity of the environmental degradation it will address)
Health Benefits	The health benefits, generally at a local level, that will be derived from the environmental improvements
Environmental Strategy	The priority of the project in the context of national and regional environmental strategies & plans (e.g. NEAP, REAP)
Environmental Impacts	Any significant environmental impacts (costs) of the project, particularly for projects that require an EIA to be carried out
Cross-Border Issues	Any wider (cross-border) environmental costs and benefits from the project
Relevant Conventions	Links to international environmental conventions, and priorities allocated in the context of those conventions

FINANCIAL CRITERIA FOR PROJECT PRIORITISATION

Criterion	*Comment/Description*
Capital Cost	The total capital investment needed to implement the project, as an indicator of the scale of the project
Operation Costs	The annual operation and maintenance costs, including staff costs, equipment, materials, taxes, indemnities etc.
Income Generated	The total expected annual income that will accrue to the project, for example from user charges and/or the sale of energy
Finance Secured	The extent to which finance has already been secured to cover the costs of the project and the type of finance mobilised
Timing of Finance	The impact of available existing sources of finance on the likely timing of the proposed project

ECONOMIC CRITERIA FOR PROJECT PRIORITISATION

Criterion	Comment/Description
Affordability of Charges	Affordability of proposed charges to those who will pay them (e.g. individual households, industry)
Collectability of Charges	Proposed charges will actually be paid, based on mechanism established for their collection
Affordability of Investment	Affordability of proposed investment (e.g. to local authority and/or government who will have to manage and pay the financing cost)
Wider Economic Benefits	Wider economic benefits of the project, for example in employment creation or stimulating inward investment
Wider Economic Costs	Wider economic costs of the project, for example jobs lost or economic output reduced

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TECHNICAL CRITERIA FOR PROJECT PRIORITISATION

Criterion	Comment/Description
Scale of Project	Scale of project (population served, water treatment capacity)
Type of Project	New facility or the replacement, extension/upgrading of an existing one
Complexity of Project	Complexity of proposed project and technologies used
Readiness of Project	Current status of project development (existing studies, project design)
Resources for Development	Available experienced staff for project development and management
Status of EIA Process	Existing EIA and public consultation
Other Permitting Issues	Existing necessary permits
Earliest Start Date	Earliest date (year) at which the project could proceed

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SOCIAL AND POLITICAL CRITERIA FOR PROJECT PRIORITISATION

Criterion	Comment/Description
Public Support/ Opposition	(Local) public support for or opposition to (e.g. NIMBY = Not In My Back Yard) the proposed project
Political Support/ Opposition	(Local) political support for or opposition to (e.g. NIMTOO = Not In My Term Of Office) the proposed project
Profile of Project	Public and media profile of the proposed project, primarily at a local level
Champion for Project	Existing influential 'project champion' promoting the proposed project

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COMMERCIAL AND INSTITUTIONAL CRITERIA FOR PROJECT PRIORITISATION

Criterion	Comment/Description
Definition of Responsibilities	Responsibilities for project development and implementation (planning, financing, construction, operation etc.) are clearly defined and understood
Legal/ Commercial/ Institutional Framework in Place	Existing the legal, institutional and commercial framework needed to implement the project is already in place
Public Private Participation (PPP)	Legal and regulatory framework for establishing and monitoring a private participation in the project is in place and operational
Competing Demands for Resources	Existing competing demands for the resources planned to be use at a local/national level from other projects/directives

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TYPICAL INDICATORS FOR DRINKING WATER AND WASTEWATER PROJECTS

- Strategy/ plan
- Directive priority
- Trans-national impact
- Institutional arrangement
- Type and scale of facility
- Status of project
- Size – investment volume
- Additional DW or WW coverage after project (additional number of beneficiaries)
- Human health benefits
- Pollution category of receiving water body
- Wider downstream impact potential
- Status of financial sources
- Current debt to equity ratio of operator
- Affordability ratio (operational ratio: aggregated income/aggregated cost – grants)

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PROJECTS PRIORITISATION CRITERIA

- Accession
- Environmental
- Financial
- Economic
- Technical
- Social & Political
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Thank you!
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Istanbul, May 2006

CLEANER PRODUCTION ACTIVITIES IN MOLDOVA

Alexandru Stratulat

Advisor for Prime Minister and Vice Prime Minister of the Republic of Moldova, Moldova
(a_stratulat@moldova.md)

Abstract

The cleaner production idea in Moldova has started to be developed after the signature in 1999 of the International Declaration on Cleaner Production (UNEP). Beginning with that date the cleaner production in Moldova started to gain ground: the principle of cleaner production was introduced in the Government's Action Plan and in the Concept of the Environment Protection. Also, a Centre for Prevention of Industrial Pollution (CPPI) (now Cleaner Production and Energy Efficiency Centre (CPEE) Centre) was established. A campaign to raise public awareness on the issues of Cleaner Production started. As a result of these efforts in September 2003 the National Declaration on Cleaner Production was adopted.

This latter has a great importance for the Moldovan government, since through the implementation of cleaner production processes it tries to achieve a series of goals:

- Pollution control and reduction of the social costs of the environment's degradation;
- Sustainable development of the industrial sector and society through cleaner production;
- Implementation of the National Strategy for Sustainable Development.

Cleaner Production in the Republic of Moldova

Alexandru Stratulat

Republic of Moldova

Istanbul, 2006

Cleaner Production in the Republic of Moldova

Brief country profile

Economy: food industry, wine industry, light industry

Today Moldova is a net energy importer, from the Russian Federation, Ukraine and Romania, with only 3% of the demand for primary energy covered by domestic sources.

The Republic spends more than 500.000.000 USD annually on energy, an amount equivalent to 29% of its GNP. About 60% of the final energy consumption is in the form of electricity and heat, of which the industry is the main consumer.

Cleaner Production in the Republic of Moldova

Introduction

1. Signature in 1999 of the International Declaration on Cleaner Production (UNEP);
2. Introduction of the principle of cleaner production in the Government's Action Plan and in the Concept of the Environment Protection;
3. Establishment in June 1999 of the Centre for Prevention of Industrial Pollution (CPPI) (now Cleaner Production and Energy Efficiency Centre (CPEE) Centre);
4. Raising of the public awareness on Cleaner Production issues;
5. Adoption of the National Declaration on Cleaner Production (September 2003).

Cleaner Production in the Republic of Moldova

Through the implementation of cleaner production processes the Government tries to achieve:

1. Pollution control and reduction of the social costs of the environment's degradation;
2. Sustainable development of the industrial sector and society through cleaner production;
3. Implementation of the National Strategy for Sustainable Development.

Cleaner Production in the Republic of Moldova

Main obstacles:

1. Human conservatism;
2. Limited awareness and understanding of the cleaner processes;
3. Financial constraints;
4. Limited human resources;
5. Lengthy decision-making process;
6. Lack of the promotion of the cleaner production ideas and technologies.

Cleaner Production in the Republic of Moldova

National Actors in the Cleaner Production field in the Republic of Moldova

1. Cleaner Production and Energy Efficiency Centre;
2. EU TACIS project "Cleaner Production in selected countries of the CIS: Kazakhstan, Georgia and Moldova" (started in 2003 and ended in 2005);
3. Ministry of Environment and Natural Resources;
4. Ministry of Agriculture and Food Industry;
5. Ministry of Industry and Infrastructure;
6. State Agency for Sylviculture "Moldsilva";
7. Technical University, Chisinau, Moldova;
8. Various Moldovan enterprises and NGOs...

International Partners:

1. OECD;
2. Norwegian Society of Chartered Technical and Scientific Professionals (former NIF);
3. Norwegian Energy Efficiency Group (NEEG);
4. Russian-Norwegian Center "Cleaner Production";
5. Polish Cleaner Production Centre;
6. Slovak Cleaner Production Centre;
7. Pollution Prevention Centre (Romania);
8. Scientific-production company "Biolant" (Russia);
9. Biotechnical Center (Latvia).

EU TACIS project "Cleaner Production in selected countries of the CIS: Kazakhstan, Georgia and Moldova"

The overall objective of the CP Tacis Project is to achieve the catalytic effect of the promotion and implementation of the Cleaner Production Strategy in the NIS countries.

The emphasis is put on:

- Simultaneous achievement of economic and environmental benefits and the integration of environmental management into mainstream management practice;
- Application of an integrated, preventive environmental strategy to production processes and to products throughout their lifecycle;
- Minimization of the risk for human health and the sustainable use of natural resources.

EU TACIS project "Cleaner Production in selected countries of the CIS: Kazakhstan, Georgia and Moldova"

Main project objective is to enhance the capability and commitment of three selected target groups to the promotion of CP:

1. Industries (CP Demo projects implementation)
2. CP Centers (achieve the Basic Capacity Level)
3. Government departments (to increase the awareness of decision makers).

EU TACIS project "Cleaner Production in selected countries of the CIS: Kazakhstan, Georgia and Moldova"

The Project Objectives:

1. Efficient industrial resource use and reduced pollution of the environment;
2. Support the development of policy framework conditions that are conducive to CP uptake;
3. Help achieve "Basic Capacity Level" in CP;
4. Increase awareness of decision makers on the economic potential of CP.

Cleaner Production and Energy Efficiency Centre

The long-term capacity building programme "Cleaner Production and Energy Efficiency (CP and EE) in Moldova" started in June 2001.

The long-term objectives of the programme are to contribute to increased energy efficiency in industries and buildings, reduced pollution loads and improved environment in the Republic of Moldova.

Capacity Building and Project Development

The following CPEE programmes have been carried out in Moldova in 2005:

1. Energy Auditing of Buildings, Training of Trainers at the Technical University in Chisinau, October 2004 - March 2005
2. Cleaner Production and Energy Efficiency, Balti, May-November 2005
3. Cleaner Production and Energy Efficiency, Floresti, April-December 2005
4. Medical Waste Management in hospitals of Moldova

Cleaner Production in the Republic of Moldova

Medical Waste Management in hospitals of Moldova

The following projects have been implemented in 2005:

1. Medical waste and introduction of non-incineration technologies in the Republic of Moldova
2. Promotion of safe Health Care Waste Management technologies
3. Environmentally safe health care waste treatment
4. Capacity building on Health Care Waste Management

Cleaner Production in the Republic of Moldova

Medical waste and introduction of non-incineration technologies in the Republic of Moldova

The project goals:

1. Organisation of an informational seminar
2. Creation of a medical waste database in order to secure monitoring and public access to this kind of information
3. Performance of the waste audits in hospitals in order to collect real data on infectious waste generation for the further development of an alternative concept of National Action Plan for Health Care Waste Management and introduction of non-incineration technologies in Moldova.

Cleaner Production in the Republic of Moldova

Promotion of safe Health Care Waste Management technologies

In cooperation with the Republican Centre for Preventive Medicine of Moldova with the support of international organization Health Care Without Harm Europe (HCWHE) and Mitchell Kapor Foundation (US) the existing situation in the hospitals of Moldova in the field of health care waste management was assessed.
CPEE Centre established contacts with more than 30 hospitals.
The surveys in 13 hospitals of Moldova were performed.
The obtained results were organized into a Data Base on Health Care Waste (http://cpee.md/frames/db/db-en.htm).

Cleaner Production in the Republic of Moldova

Environmentally safe health care waste treatment in Moldova

Within the framework of the project a situation analysis was develop and publish, including the quantitative and qualitative evaluation of the health care waste management in the hospitals of Moldova, and legislative and institutional framework, regulating the activities in this field, was reviewed.

Waste audits in 5 hospitals of Moldova were conducted within the framework of the project with the view of assessment of waste generation factors and collection of data for 25 categories of waste.

Cleaner Production in the Republic of Moldova

Capacity building on Health Care Waste Management

Within the framework of the project the existing health care waste management legislation and regulations were evaluated, recommendations on their adjustment to the European standards were issued and a draft of the National Strategy for Health Care Waste Management was developed.

International partners, NGOs and domestic health and environment authorities were involved into the implementation of the project.

Cleaner Production in the Republic of Moldova

Cleaner Production and Energy Efficiency Investment Project (Floresti)

Companies involved: **4**
Identified CP&EE measures: **46**
Implemented CP&EE measures: **10**
Total investments: **32.000 USD**
Sources: operational budget of the companies
grants from the TACIS project
loans from the Revolving Fund

Total investments in 2005: **521.000 USD**

Cleaner Production in the Republic of Moldova
Following steps:
1. Implementation of the National Declaration on Cleaner Production;
2. Promotion of the cleaner production in all sectors of Moldovan economy;
3. Coordination of the Cleaner Production projects, implemented in different sectors;
4. Investment attraction for the implementation of the Cleaner Production projects.

Republic of Moldova
Thank you!

FACTORS BEHIND CLEANER PRODUCTION IN THE HUNGARIAN MANUFACTURING INDUSTRY - RESULTS OF A SURVEY

Gabor Harangozo

Hungarian Cleaner Production Centre, Corvinus University of Budapest, Budapest, Hungary (

Abstract

The presentation is based on the results of an international survey carried out with the support of the OECD. Its main focus is to give a brief review on the practices used within the Hungarian manufacturing industry regarding environmental actions (wastewater management, material efficiency etc.), especially cleaner production.

It can be mentioned that cleaner production and pollution prevention is getting much more important than conventional environmental practices such as end-of-pipe technologies. Beyond the cleaning of the production technologies, the improvement of the environmental characteristics of products is getting more important, too.

The presentation also aims to examine the role of different factors - such as size, industry, the pressure of different stakeholders etc. - on the attitude and concrete actions of the manufacturing firms regarding cleaner production. An important question is whether the high level of the corporate environmental management leads to an improvement in the field of concrete environmental actions and cleaner production.

A key element of the analysis is the effectiveness of the environmental actions carried out by the firms, to what extent they contribute to the decrease of the environmental impacts of companies.

Last but not least, the relationship between the environmental actions, the cleaner production practices and the general business performance of the firms is analysed.

Factors behind cleaner production in the Hungarian manufacturing industry

Results of a survey

Gábor Harangozó
Corvinus University of Budapest
11.05.2006

Structure of the presentation

- Introducing the survey and the sample
- Environmental actions and cleaner production at the Hungarian firms
- The role of the environmental management
- The effectiveness of the environmental actions
- Relationship between environmental and business performance
- Conclusion

Represented sectors, frequencies and rates of respondents

NACE-code	Manufacturing sector	Ground population*	Total sample*	Responses	Response rates*
15	Food and beverages	588	252	69	27,4%
16	Tobacco	5	4	1	25,0%
17	Textile	122	80	13	16,3%
18	Wearing	276	162	26	16,0%
19	Leather	97	65	11	16,9%
20	Wood	80	42	15	35,7%
21	Paper	45	30	8	26,7%
22	Printing	83	48	12	25,0%
23	Fuel	2	2	2	100,0%
24	Chemicals	80	53	21	39,6%
25	Rubber and plastics	157	80	33	41,3%
26	Non-metallic mineral	104	70	25	35,7%
27	Basic metals	56	36	12	33,3%
28	Fabricated metal	283	146	41	28,1%
29	Other machinery	214	134	51	38,1%
30	Office machinery	13	9	2	22,2%
31	Electrical machinery	114	84	37	44,0%
32	Radio, television	79	63	21	33,3%
33	Medical instruments	49	33	14	42,4%
34	Motor vehicles	74	61	14	23,0%
35	Other transport equipment	25	18	8	44,4%
36	Manufacturing n.e.c.	104	54	13	24,1%
37	Recycling	7	4	3	75,0%
	Other or missing			14	
	All manufacturing sectors	2417	1530	466	30,5%

Introducing the survey and the sample
- **Environmental actions and cleaner production at the Hungarian firms**

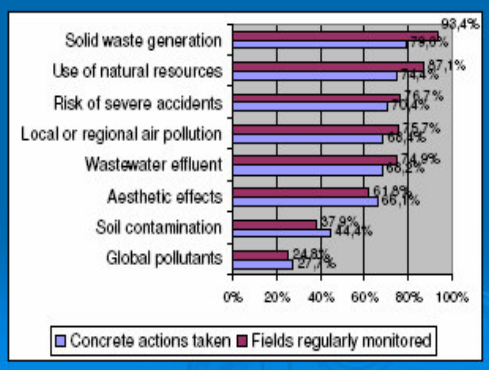
The role of the environmental management

The effectiveness of the environmental actions

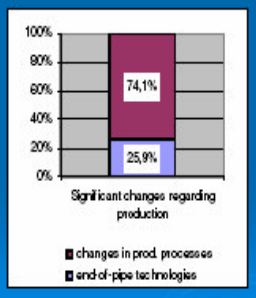
Relationship between environmental and business performance

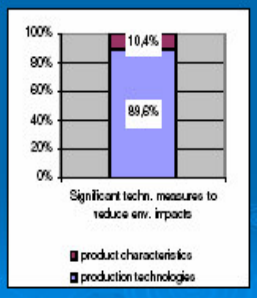
Conclusion

Environmental actions taken by the firms

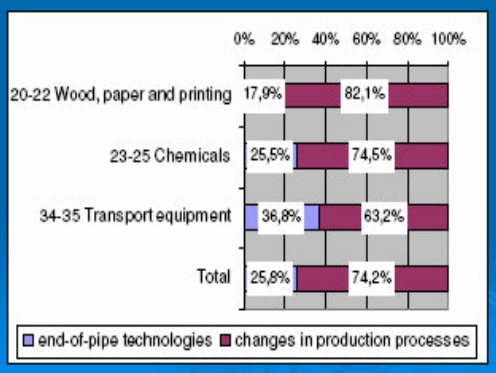


Characterising the actions made to reduce environmental impacts

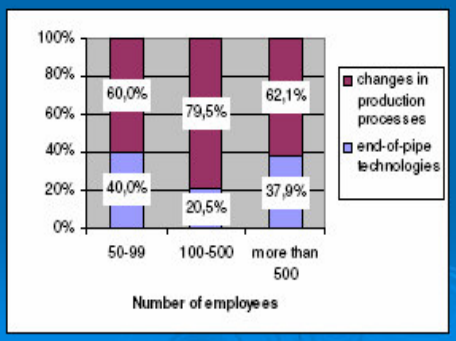




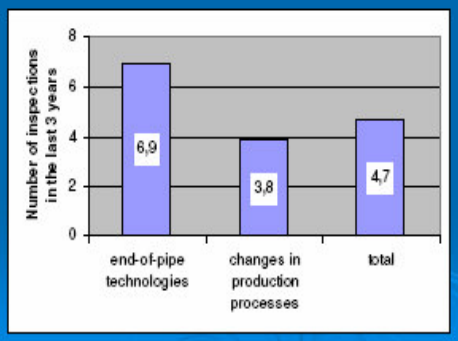
Characteristics of environmental actions by activity



Characteristics of environmental actions by size (number of employees)



Characteristics of environmental actions by the frequency of authority inspections



Introducing the survey and the sample

Environmental actions and cleaner production at the Hungarian firms

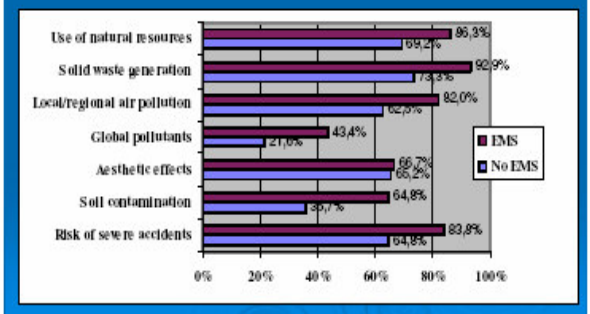
➢ **The role of the environmental management**

The effectiveness of the environmental actions

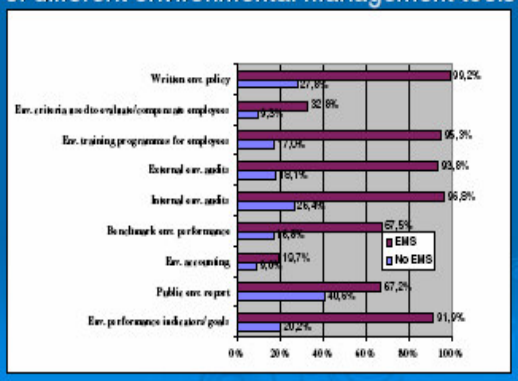
Relationship between environmental and business performance

Conclusion

The relationship between environmental actions and the introduction of an EMS

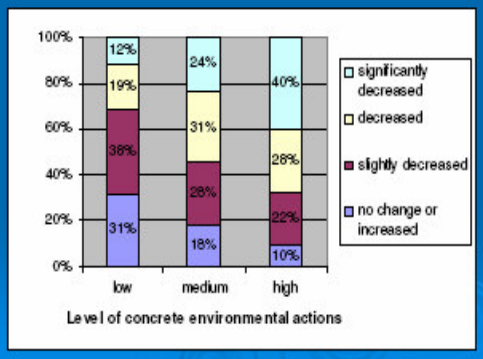


The relationship between EMS and the use of different environmental management tools

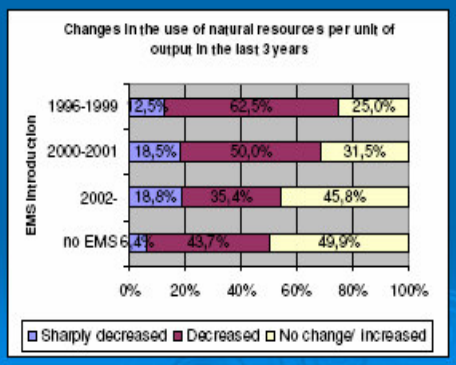


Introducing the survey and the sample
Environmental actions and cleaner production at the Hungarian firms
The role of the environmental management
➢ **The effectiveness of the environmental actions**
Relationship between environmental and business performance
Conclusion

The effects of the environmental actions on the env. impacts per unit of output

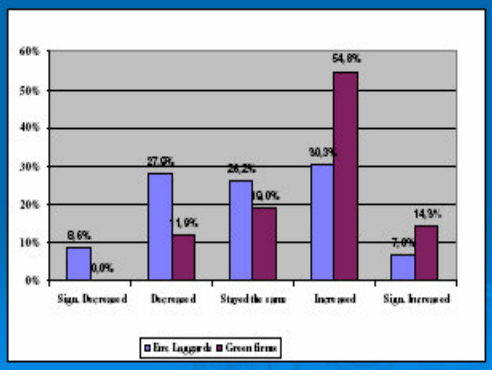


An example: the temporal effects of EMS

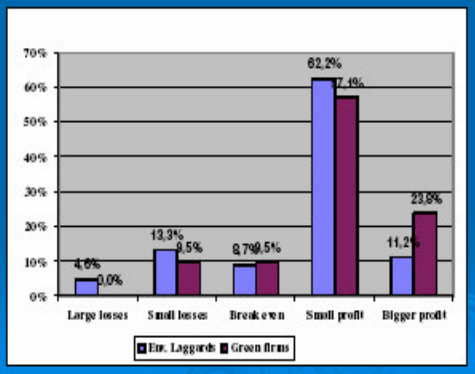


Introducing the survey and the sample
Environmental actions and cleaner production at the Hungarian firms
The role of the environmental management
The effectiveness of the environmental actions
➢ **Relationship between environmental and business performance**
Conclusion

Green firms' and environmental laggards' changes in value of shipment in the past 3 years



Green firms' and laggards' economic performance



Conclusion/1.

- Difference between industries regarding cleaner production
- Medium-size firms seem to be the most innovative
- Too stringent regulation might not always support cleaner production

Conclusion/2.

- EM supports cleaner production
- Concrete environmental actions resulted to be effective
- Green firms seem to be more successful in other fields as well

Thank You for your attention!

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CARBON DIOXIDE EMISSIONS IN SPAIN: MAIN SOURCES AND CAPTURE POSSIBILITIES

Miguel Ángel Suárez, Eva Díaz and José Coca

Department of Chemical Engineering and Environmental Technology
University of Oviedo, 33006 Oviedo, Spain (jcp@uniovi.es)

Abstract

A brief review the main sources of CO_2 –mainly stationary sources- and energy conservation strategies in Spain is made. The documents issued and actions taken in order to reduce CO_2 emissions, in order to comply with the Kyoto protocol, are also considered. The available technologies for CO_2 reduction, depending on the emission source, have also been included.

Keywords: *Greenhouse gases, CO_2 capture, Spain*

NATO/CCMS Clean Products and Processes
Istanbul (Turkey) May 8-12, 2006

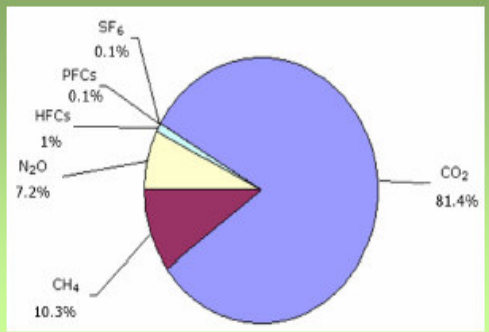
CARBON DIOXIDE EMISSIONS IN SPAIN: MAIN SOURCES AND CAPTURE POSSIBILITIES

Miguel Ángel Suárez
Eva Díaz
José Coca

INTRODUCTION

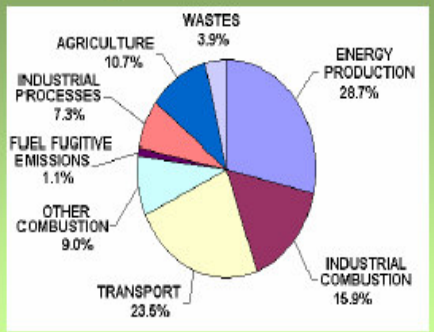
- CO_2 emissions: *greenhouse* effect
- Kyoto protocol: agreement of different countries to reduce CO_2 emissions
- Spain:
  - 2008-2012: increase of 15 % respect 1990
  - 2003: increase of **41 %**
- Measures to reduce emissions:
  - "*National Plan of Emissions Assignment*" (2004)

CO_2 EMISSIONS IN SPAIN



GASES

CO_2 EMISSIONS IN SPAIN



SECTORS

SOURCES OF CO_2 IN SPAIN

- Energy production:
  - 50 % of electric power is obtained in thermoelectric power plants
  - General trend: improve process efficiency
  - Other alternatives:
    - Renewable energies
    - Precombustion
    - Oxyfuel combustion

SOURCES OF CO_2 IN SPAIN

- Industrial sector:
  - Cement industry
    - Clinker production: 0.72 t CO_2/t clinker
    - Trends:
      - Raw materials with low organic matter
      - Absorption (MEA) is the most common method of CO_2 sequestration
      - PSA and TSA are becoming commercial technologies
- Other industrial sectors
  - Iron, steel, refining, etc.
  - General trend: increase process efficiency

SOURCES OF CO_2 IN SPAIN

- Transportation sector:
  - No capture technologies available
  - Recommendations:
    - Use of natural gas, gas-oil or propane instead of gasoline as fuel
    - *Biodiesel*
- Agriculture and forestry
  - Act as carbon dioxide sinks
  - 0.67 million t CO_2/ year for Spain
- Residential
  - Energy conservation

NETWORKING SATELLITE GROUNDSTATIONS TO SUPPORT GLOBAL SCIENCE: TOWARD A DISTRIBUTED SHARED SPATIAL DATA ARCHIVE & GRID ACCESS TO NEAR-REAL-TIME REMOTE SENSING DATA

Gilbert L. Rochon[1], Virgil Sharpton[2] and Okan K. Ersoy[3]

[1] *Associate Vice President for Collaborative Research, Director of Purdue Terrestrial Observatory, Purdue University , W. Lafayette, IN, USA,*
(rochon@purdue.edu),
[2]*Geographic Information Network of Alaska, University of Alaska Fairbank,*
(buck.sharpton@alaska.edu),
[3]*Purdue University (ersoy@purdue.edu)*

Abstract

It has been estimated that twenty countries will have mid to high resolution earth observing satellites in orbit by 2010 (Stoney, 2005)[A]; however, only a very few institutions of higher learning, world-wide, maintain groundstations capable of receiving real-time satellite data from multiple sensors. Given that anthropogenic and biogenic disasters have not always confined themselves to nation-state boundaries, and given that global climate research, oceanography, coastal zone morphology, global deforestation, agricultural pest infestation, epidemics, epizootics, atmospheric sciences and comparative megacity research, inter alia, all require access to archival and near-real-time international data, it is incumbent upon academic groundstations to collectively strive to establish a distributed shared archive of satellite data and access to near-real-time remotely sensed data.

As a prelude to accomplishing this objective, several universities and research institutes in Turkey have indicated their interest in forming a coalition to serve as an integrated node and Center of Excellence for Applied Spatial Data Research within a Global Grid for Archival and Real-time Remote Sensing **(G^2AR^2S).** Thus far, the coalition includes Istanbul Technical University, Middle East Technical University, Bogazici University, Kandilli Observatory, Aeronautics & Space Technology Institute and Marmara University. Based upon the Turkish prototype, the objective is to identify or form analogous collectivities in Europe, Asia, Latin America and Canada. Within the USA, a possible precursor would be the AmericaView Program, currently funded by the United States Geological Survey (USGS). AmericaView is an amalgam of twenty State Consortia developed for the purpose of enhancing access to archival remotely sensed data. Groundstations for real-time remote sensing, located in five AmericaView member states (i.e. Indiana, Louisiana, Texas, California & Alaska) could form the initial basis for dissemination of near-real-time data to the others. Rapid dissemination can be facilitated by the fact that three of the groundstations (i.e. Purdue Terrestrial Observatory at Purdue University in Indiana; University of Texas at Austin and the Scripps Institute of Oceanography at the University of California San Diego) are also nodes on the National TeraGrid, a high bandwidth backbone, supported by grants from the National Science Foundation.

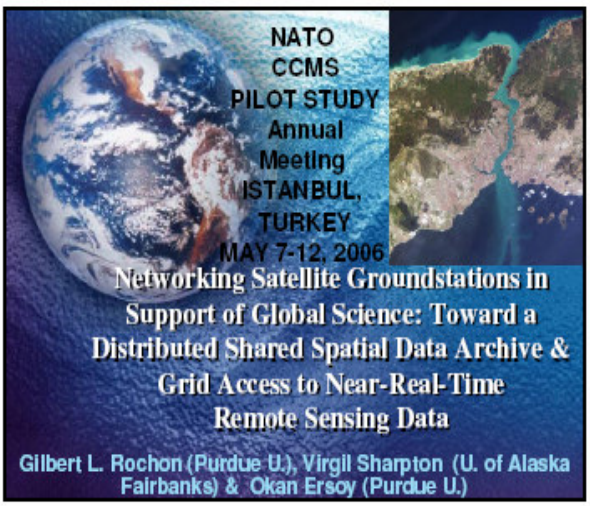
The authors have previously presented a scenario for establishment of "NATO View,"[B] wherein member countries would benefit from subsidized access to their respective archives of satellite data, as do members of AmericaView. Previous presentations also addressed the benefit of such an approach for the African continent.[C] The authors now present a viable scenario for a global archival and real-time remote sensing grid, which would link the satellite groundstation in Istanbul

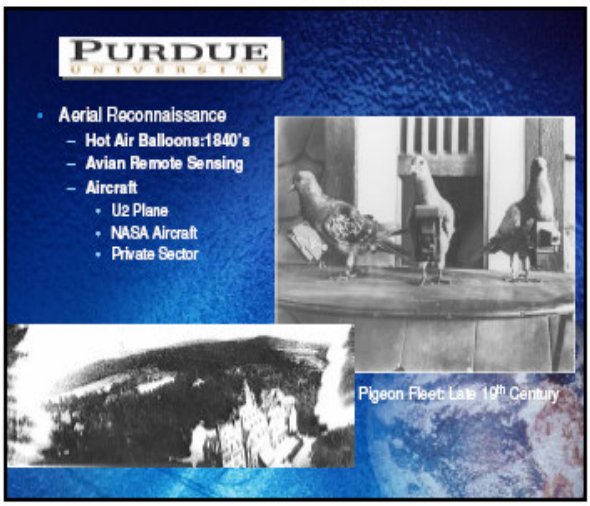
and cooperating universities and research institutions in Turkey with their counterparts in Singapore, Europe, Africa, Asia, Russia, South America, Canada and the USA.

[A] Stoney, William E. Guide to Land Imaging Satellites. Mitretek Systems, Bethesda, MD: ASPRS, 2005 http://www.asprs.org/news/satellites/

[B]Virgil L. Sharpton & Gilbert L. Rochon. Invited presentation, "Archival and Real-Time Satellite Remote Sensing in Support of Environmental Sustainability within NATO Countries: Toward NATO View," North Atlantic Treaty Organization (NATO) Committee on the Challenges to Modern Society (CCMS) Pilot Study on Clean Products & Processes Phase II, June 17-15, 2005, Alesund, Norway

[C]Gilbert L. Rochon, J. Quansah, M. Mohamed, Y. Twumasi, T. Coleman, V. Taylor, C. Luther, C. Johannsen and D. Landgrebe. "Applicability of Near-Real-Time Satellite Data Acquisition and Analysis and Distribution of Geo-information in Support of African Development," United Nations Economic Commission for Africa (UN ECA) Committee for Development Information (CODI IV) Addis Ababa, Ethiopia, April, 2005.


NATO
CCMS
PILOT STUDY
Annual
Meeting
ISTANBUL,
TURKEY
MAY 7-12, 2006
Networking Satellite Groundstations in Support of Global Science: Toward a Distributed Shared Spatial Data Archive & Grid Access to Near-Real-Time Remote Sensing Data
Gilbert L. Rochon (Purdue U.), Virgil Sharpton (U. of Alaska Fairbanks) & Okan Ersoy (Purdue U.)


PURDUE UNIVERSITY
Aerial Reconnaissance
– Hot Air Balloons:1840's
– Avian Remote Sensing
– Aircraft
• U2 Plane
• NASA Aircraft
• Private Sector
Pigeon Fleet: Late 19th Century

PURDUE UNIVERSITY
AVIRIS
NASA Wallops Island
Hot Air Balloon
NASA Stennis Lear Jet
Airborne remote sensing has heretofore been the method of choice for high resolution over flights, utilizing experimental sensors & pre-launch testing of precursor instrumentation.
CALIBRATED AIRBORNE MULTISPECTRAL SCANNER (CAMS)

PURDUE UNIVERSITY
U2 Spy Plane Versions-Lockheed
Fargo, North Dakota-
Image taken by U2

PURDUE UNIVERSITY
CORONA
LAUNCH & RECOVERY SEQUENCE
Satellite: 6-8ft.resolution approved by Eisenhower-1958 Declassified by Clinton-1995. 850,000 images: 1960-1972:Corona, Lanyard & Argon
Remains of Fort Walls

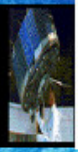
PURDUE UNIVERSITY
Orbiting Satellites
– Military
– Communications
– Astronomy
– Geo-positioning
• Global Positioning System (GPS) - USA
• GLONASS - Russia
• Galileo – European Space Agency (ESA)
– Earth Observation
Galileo: 30 satellites, orbiting at 23,616 km – Medium Earth Orbit (MEO), with real-time 1-m positioning accuracy, expected to be fully operational in 2008

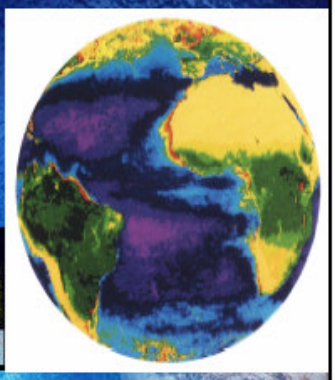
PURDUE UNIVERSITY

- Earth Observing Satellites: A Brief History

1958-1967

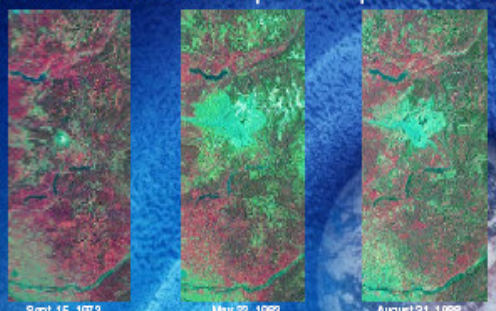
The TIROS Program





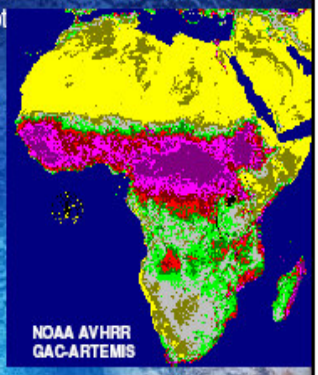
PURDUE UNIVERSITY

- Mount Saint Helens Eruption Sequence: MSS



PURDUE UNIVERSITY

- DOC NOAA- US Dept of Commerce, National Oceanic & Atmospheric Agency
  - Landsat
  - AVHRR HRPT
    - GAC
    - LAC
  - GOES



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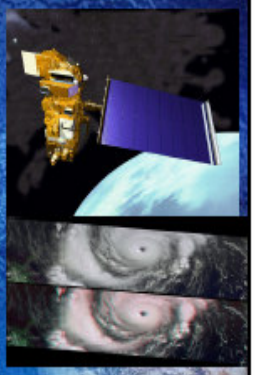
- NASA's EOS Terra
  - ASTER-Advanced Spaceborne Thermal Emission & Reflection Radiometer
  - MODIS-Moderate Resolution Spectro-Radiometer
  - CERES-Clouds & the Earth Radiant Energy System
  - MOPITT- Measurements of Pollution in the Troposphere
  - MISR- Multi-Angle Imaging Spectroradiometer (Hurricane Lili-Off Louisiana Coast, Oct. 10, 2002)



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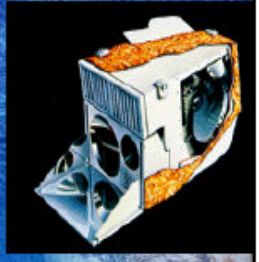
http://modland.nascom.nasa.gov/gallery/_2K0sia.A2000097.0235.523x1073.jpg

MODIS Image: April 6, 2000

Korea

36 Bands

Moderate Resolution Imaging Spectro-Radiometer (MODIS)



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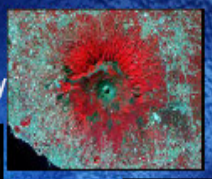
- Earth Observing Satellites: The Current Array

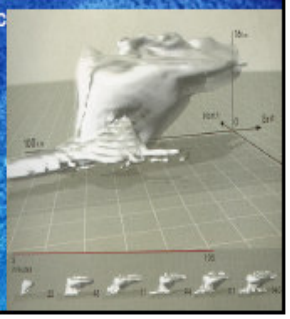


Mount Vesuvius, Italy -ASTER

Landsat 7: Namibia Kuiseb River, Aug. 26,1999. Forms the northern border of the world's largest sand dunes.

PURDUE UNIVERSITY

- NASA
  - 2004- Aura: Tropospheric & Stratospheric Atmospheric Chemistry
  - 2004- Cloudsat: 3D Cloud Profiles
  - CALIPSO: 3D Aerosol Profiles



Diversity in Space: Proliferation of National & Multinational Earth Observing Satellites

- European Space Agency
- Canada
- France
- Russia
- Japan
- China
- Korea
- Argentina
- Brazil & China
- Nigeria, Tunisia, Algeria
- South Africa & Belgium
- Turkey
- Israel

Remote Sensing Diversity:

- **CONAE (Argentina) – Sac-C**
- **Tubitak (Turkey)- EURASIASAT-1**
- **INPE (Brazil) – CBERS** (Chinese Brazilian Earth Resource Satellite)
- **CNSA (China) -Feng Yun**
- **ISA (Israel)** –EROS (Res. 1.8m; 480 km orbit, 3-7 day revisit, depending upon latitude)
- **NigeriaSat I (Nigeria)**
- **Morocco: Zarca Eliya Mama**
- **Multi-sensor Microsatellite Imager (MSMI) (Belgium & South Africa)** The three types of detectors are:
  1. A line scan multispectral detector with better than 5 meter spatial resolution and at least 3 bands: green, red and near-infrared, compatible to SPOT 4 bands.
  2. A hyperspectral detector with better than 15 meters spatial resolution and more than 200 spectral bands, ranging from 400 nanometers to 2.35 micrometers.
  3. A matrix continuous video detector with better than 10meters spatial resolution.

Satellite Proliferation

- 13 Countries now have mid to high resolution earth observing satellites in orbit
- 20 Countries will have orbiting earth observing satellites by decade's end. (W.E. Stoney, Miratek Systems)
- Radar, Panchromatic, Multispectral, Hyperspectral & Very High Resolution

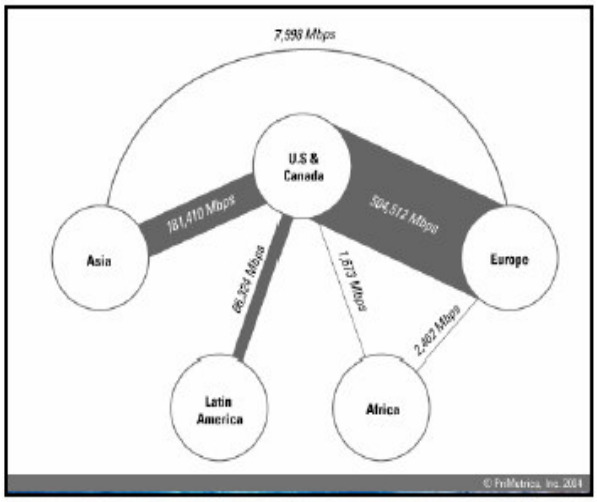
Equal Opportunity Technology: Applications in Africa, Asia & Latin America

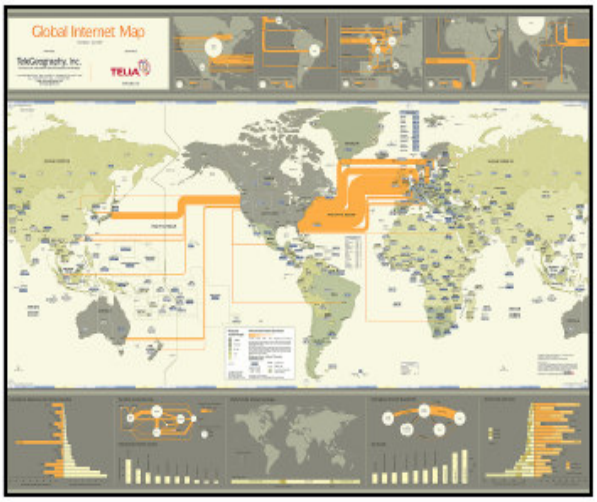
- Famine Early Warning (FEWS) Project & Food Security
- Africa Real-Time Environmental Monitoring Information System (ARTEMIS)
- African Association for Remote Sensing of Environment (AARSE)
- Precision Agriculture & Water Resources Conservation
- Coastal Zone Morphology
- Regional Impact of Climate Change
- Forest Resource Assessment
- Biodiversity & Natural Resource Management
- Sustainable Industrial Development Infectious Disease Vector Habitat Identification

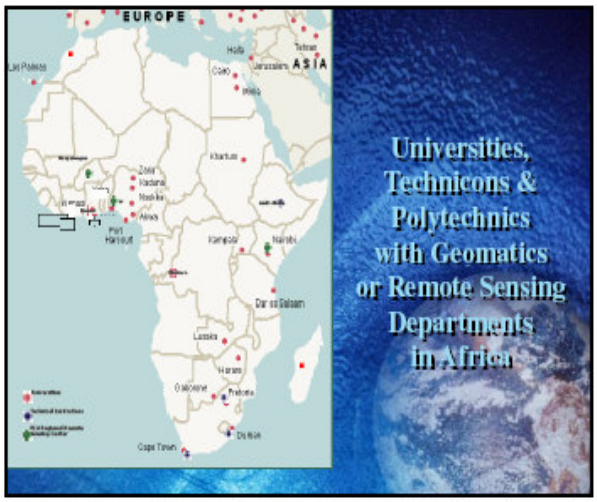
Africa and the Internet

Florence Parent, MD, MPH; Yves Coppieters, MD, MPH; Marc Parent, MD. Information Technologies, Health, and Globalization: Anyone Excluded? Journal of Medical Internet Research. Vol. 3, No. 1, Article e11, 2001.

"…there are currently more Internet users in New York City than on the entire African continent."

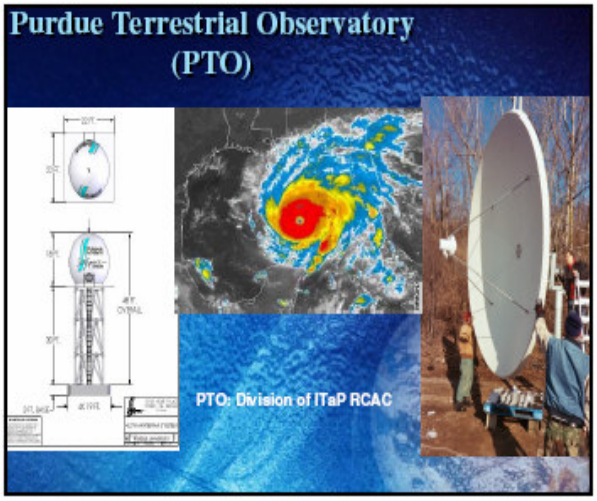




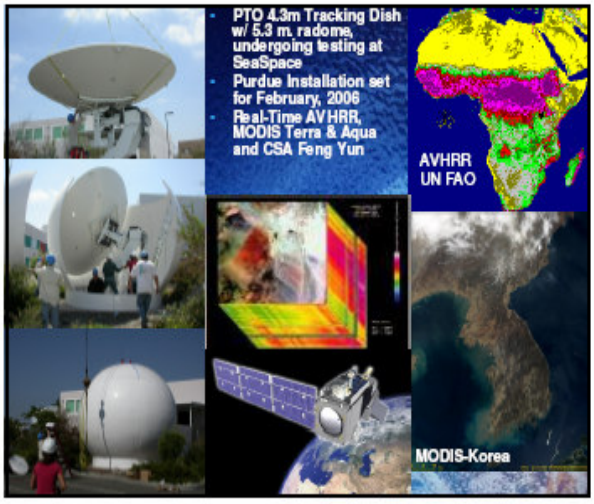


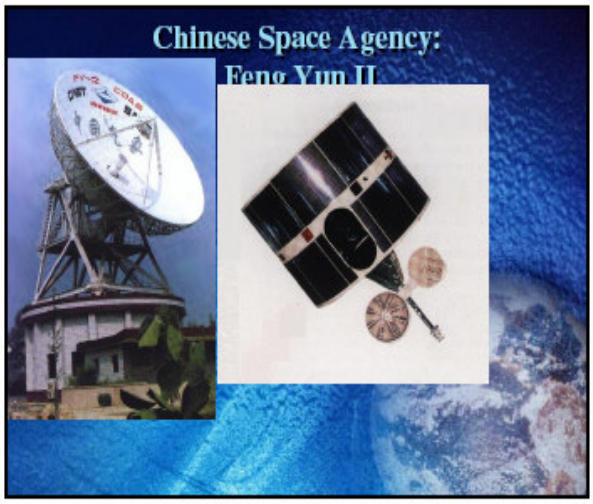
PURDUE UNIVERSITY

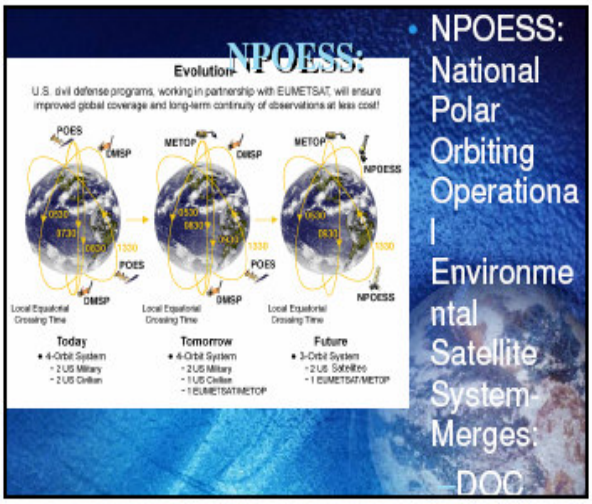
- Partial Listing: Real-Time Remote Sensing University-Based Facilities in the USA
  - Alaska Satellite Facility (U. of Alaska-Fairbanks)
  - University of Wisconsin at Madison
  - University of Miami Rosenstiel School of Marine Science
  - Louisiana State University (LSU)
  - Scripps Institute of Oceanography
  - University of Texas at Austin
  - Purdue University:
    The Purdue Terrestrial Observatory (PTO)

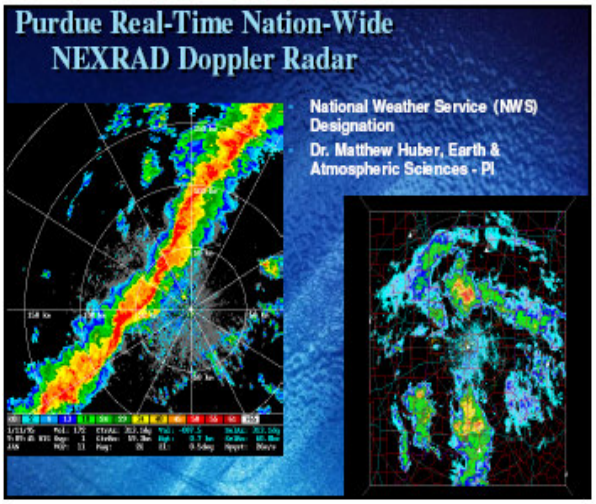


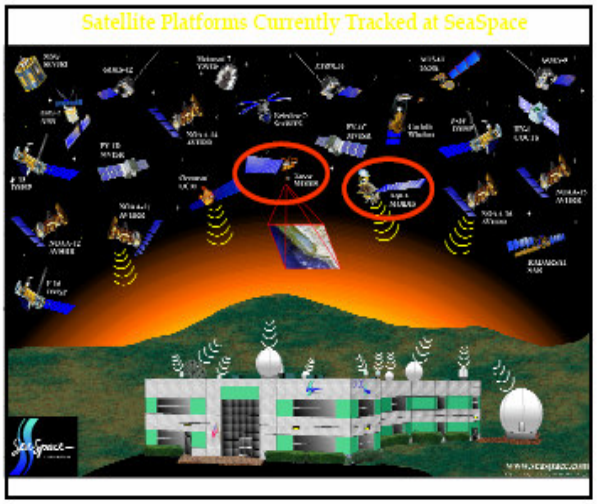
GOES: Dedicated Receiving Station 24/7
"The training I received opened my eyes & helped Convince me to attend Graduate School to pursue a doctorate."
-Cliff Robinson, III
Texas Southern University
Purdue Communications Dish Farm

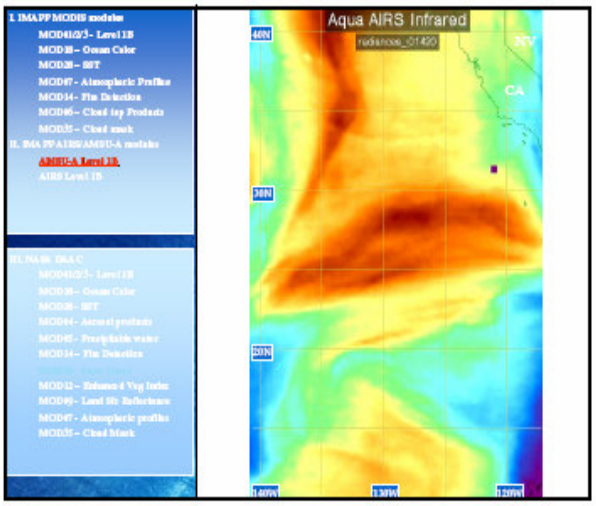

PTO 4.3m Tracking Dish w/ 5.3 m. radome, undergoing testing at SeaSpace
Purdue Installation set for February, 2006
Real-Time AVHRR, MODIS Terra & Aqua and CSA Feng Yun
AVHRR UN FAO
MODIS-Korea

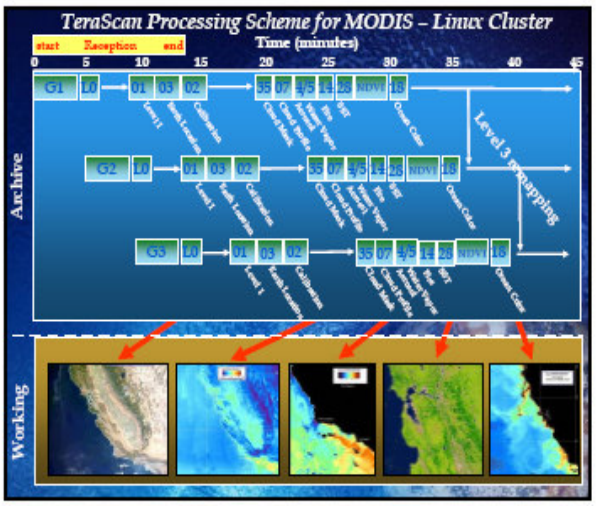

Chinese Space Agency:
Feng Yun II

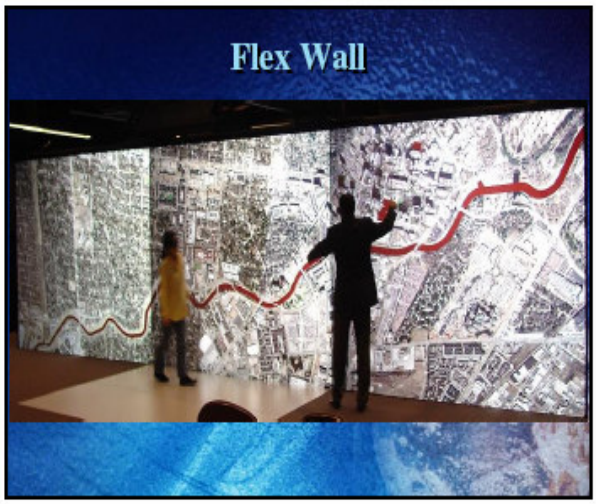

NPOESS:
Evolution
U.S. civil defense programs, working in partnership with EUMETSAT, will ensure improved global coverage and long-term continuity of observations at less cost!
POES
DMSP
METOP
NPOESS
Local Equatorial Crossing Time
Today
4-Orbit System
2 US Military
2 US Civilian
Tomorrow
4-Orbit System
2 US Military
1 US Civilian
1 EUMETSAT/METOP
Future
3-Orbit System
2 US Satellites
1 EUMETSAT/METOP
NPOESS: National Polar Orbiting Operational Environmental Satellite System- Merges: DOC


Purdue Real-Time Nation-Wide
NEXRAD Doppler Radar
National Weather Service (NWS) Designation
Dr. Matthew Huber, Earth & Atmospheric Sciences - PI

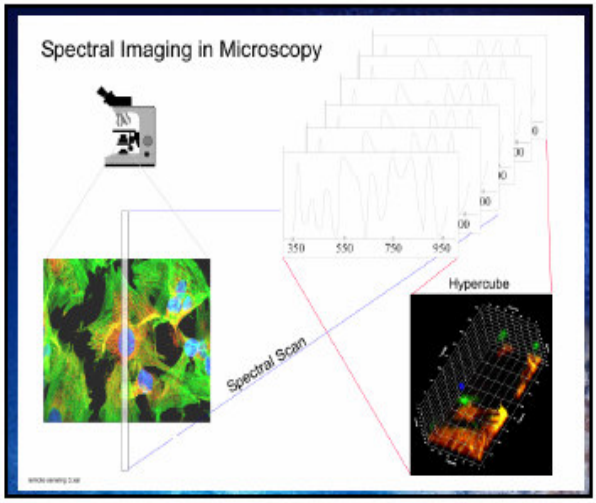

Satellite Platforms Currently Tracked at SeaSpace

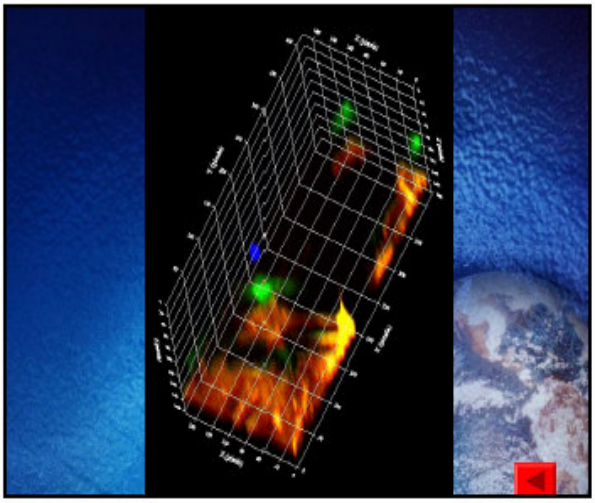

Aqua AIRS Infrared
CA

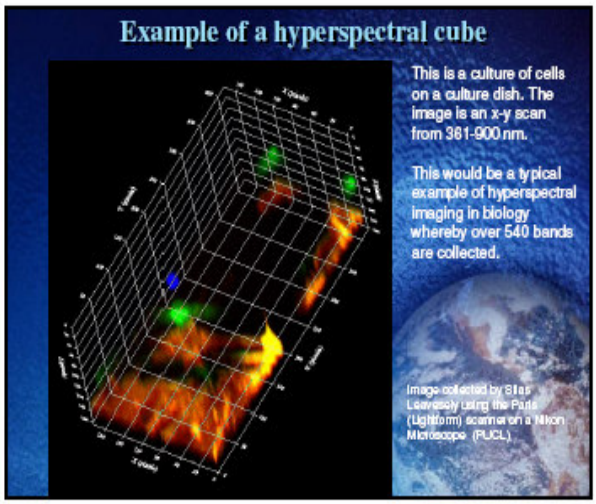

TeraScan Processing Scheme for MODIS – Linux Cluster
start
Reception
end
Time (minutes)
0
5
10
15
20
25
30
35
40
45
Archive
Working
Level 3 remapping

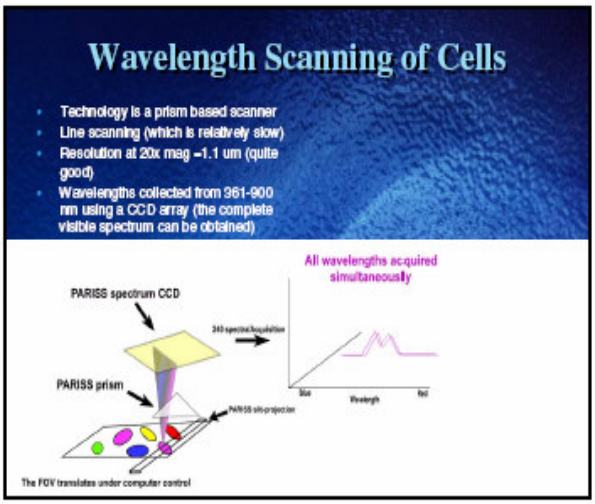

Flex Wall

AMERICA VIEW
Member Organizations:
INDIANA VIEW
Ball State University - Muncie
Indiana State University - Terre Haute
IUPUI - Indianapolis
Indiana University – Bloomington
Indiana University – South Bend
Martin University – Indianapolis
Purdue University – West Lafayette
Purdue University – Calumet
University of Notre Dame – South Bend
Indiana Geological Survey (IGS)
Indiana Geographic Information Council (IGIC)
Indiana Space Grant Consortium (ISGC)
Vincennes University
Coalition of Universities for Spatial Information Sciences (CUSIS)

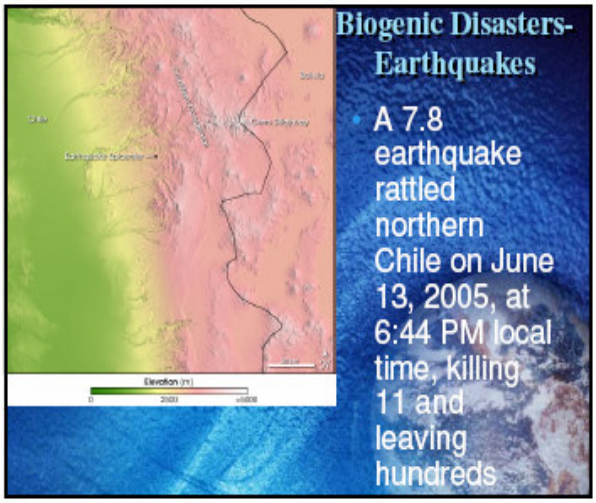

Spectral Imaging in Microscopy
350
550
750
950
Hypercube
Spectral Scan

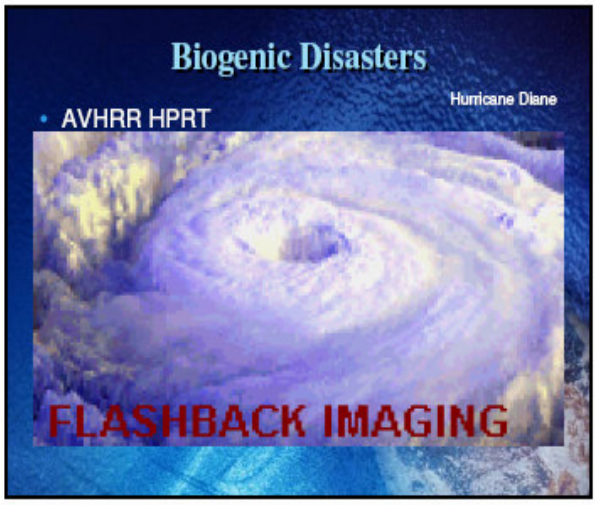



Example of a hyperspectral cube
This is a culture of cells on a culture dish. The image is an x-y scan from 361-900 nm.
This would be a typical example of hyperspectral imaging in biology whereby over 540 bands are collected.
Image collected by Silas Leavesley using the Paris (Lightform) scanner on a Nikon Microscope (PUCL)

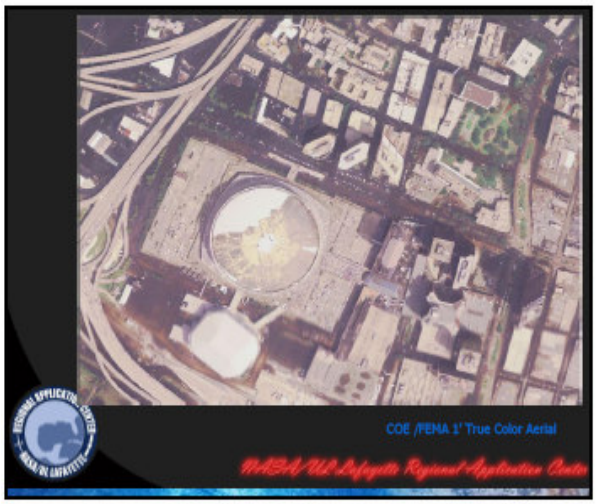

Wavelength Scanning of Cells
Technology is a prism based scanner
Line scanning (which is relatively slow)
Resolution at 20x mag ~1.1 um (quite good)
Wavelengths collected from 361-900 nm using a CCD array (the complete visible spectrum can be obtained)
All wavelengths acquired simultaneously
PARISS spectrum CCD
PARISS prism
The FOV translates under computer control

PURDUE
UNIVERSITY
Vegetation Change Detection
January


Biogenic Disasters-
Earthquakes
• A 7.8 earthquake rattled northern Chile on June 13, 2005, at 6:44 PM local time, killing 11 and leaving hundreds

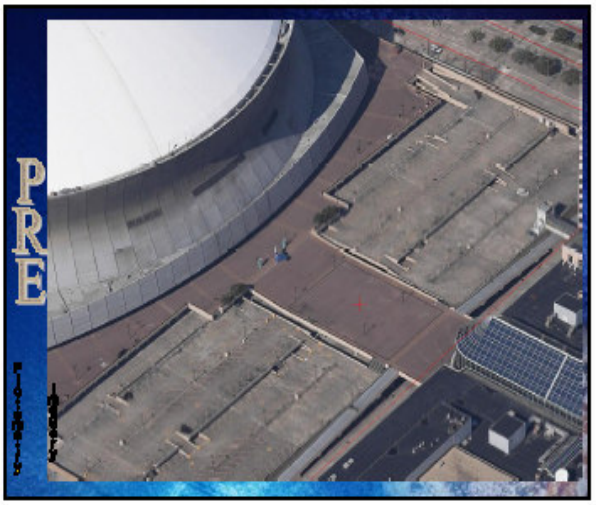

Biogenic Disasters
Hurricane Diane
• AVHRR HPRT
FLASHBACK IMAGING

Aerial Photography
1973 Aerial Photography

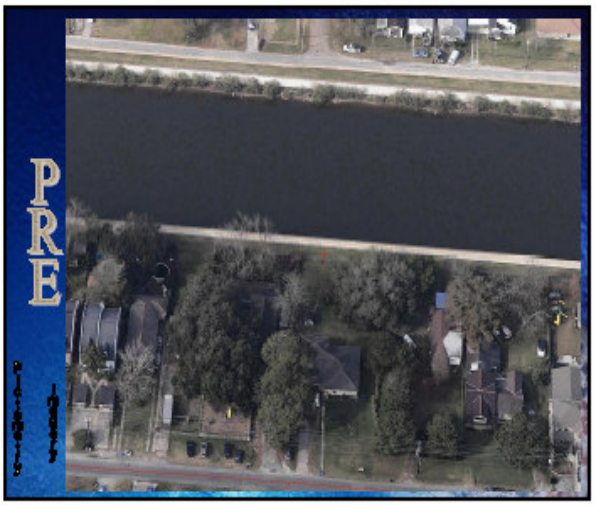

COE /FEMA 1' True Color Aerial

PRE

POST


PRE

POST


PRE

POST

PRE

POST

PRE

POST

PRE

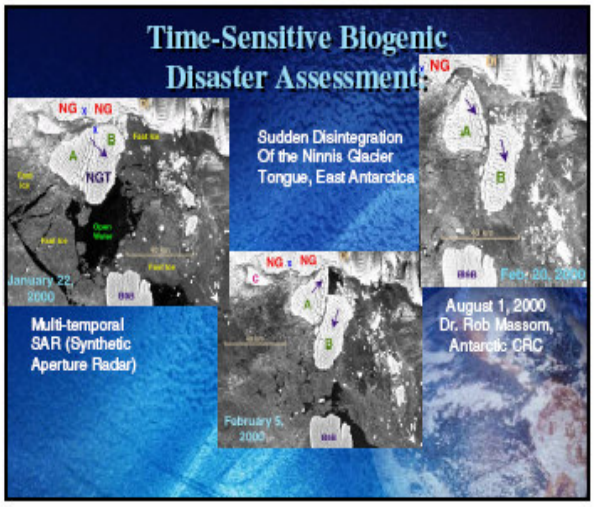
POST

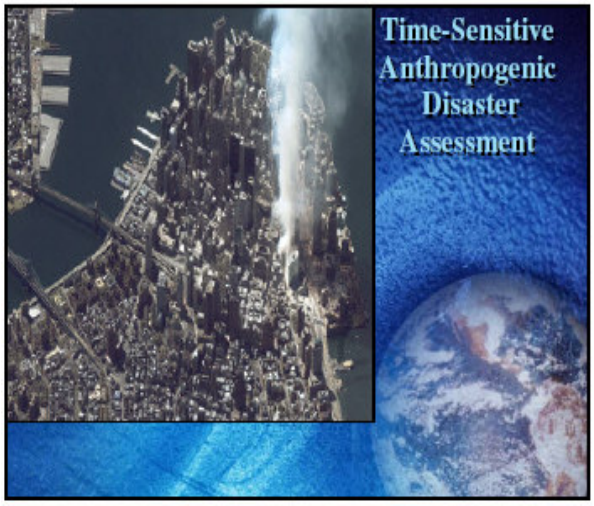
PRE

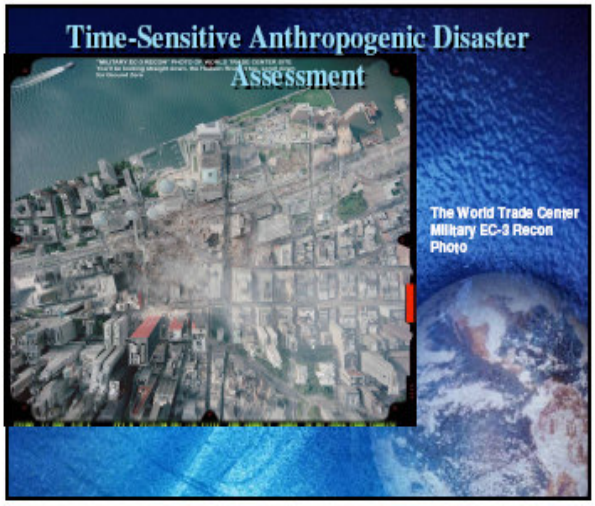
POST

PRE

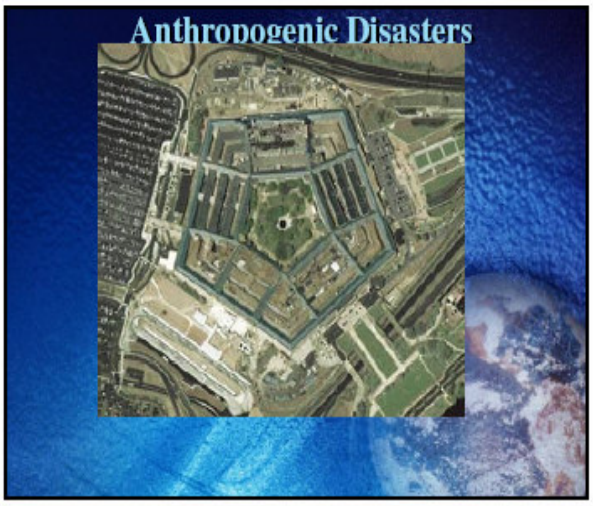
POST

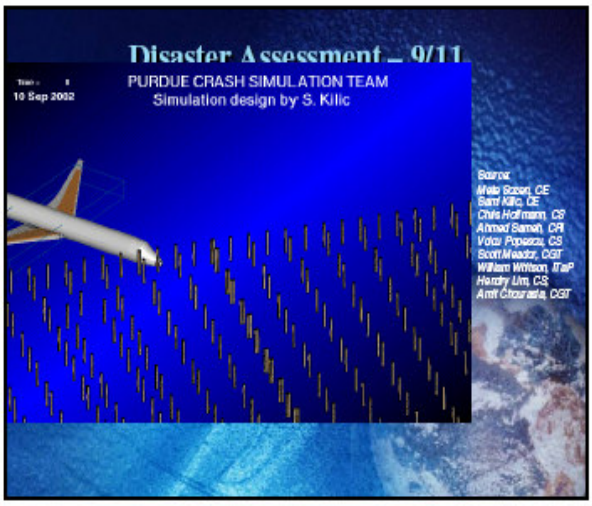

Time-Sensitive Biogenic Disaster Assessment
Sudden Disintegration Of the Ninnis Glacier Tongue, East Antarctica
Multi-temporal SAR (Synthetic Aperture Radar)
August 1, 2000
Dr. Rob Massom, Antarctic CRC

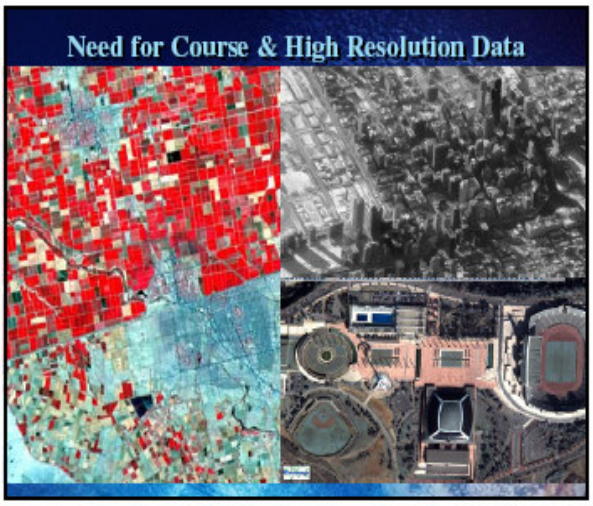

Time-Sensitive Anthropogenic Disaster Assessment


Time-Sensitive Anthropogenic Disaster Assessment
The World Trade Center Military EC-3 Recon Photo

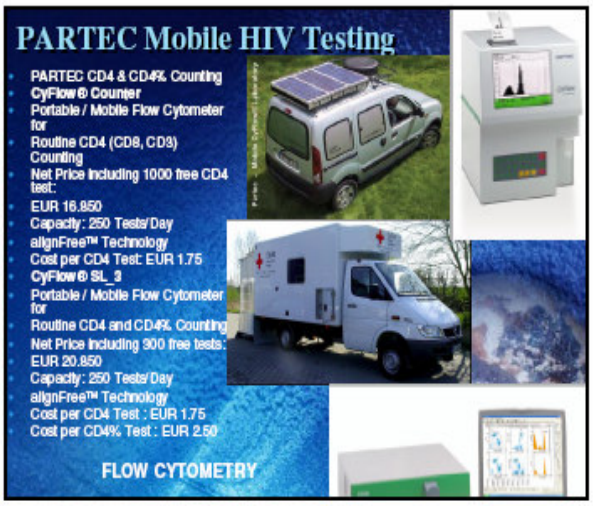
Ground Zero


Anthropogenic Disasters


Disaster Assessment – 9/11
10 Sep 2002
PURDUE CRASH SIMULATION TEAM
Simulation design by S. Kilic
Source:
Melis Sozen, CE
Sami Kilic, CE
Chris Hoffmann, CS
Ahmad Sameh, CR
Voicu Popescu, CS
Scott Meador, CGT
William Wilson, ITaP
Hendry Lim, CS
Amit Chourasia, CGT

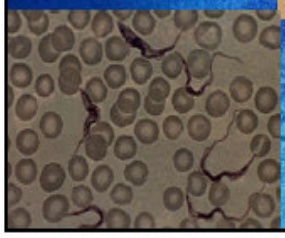

Need for Course & High Resolution Data

Hand Held Computers:
http://p3international.org/projects/
P3 Project – Hong Kong What does P3 do?
Far from the information economy, millions of families live in crushing poverty, without access to basic health care, economic opportunity, education and agricultural information. They live without email or other access to those with the resources and commitment to help. P3 is a Hong Kong based initiative, affiliated with Crossroads International, to place those necessities in the hands of those battling dire need. In our pilot projects, we recycle older Palms for the world's largest, poorest people groups and equip them, in their own language, with information for:
education (primarily for children)
literacy (for all ages)
economic opportunities (to help them build small businesses)
health care, food & nutrition
agriculture
basic email
http://village.crossroadsint.org/index.cfm/page/p3
In later phases, P3 will seek to develop and manufacture an ultra cheap handheld "information appliance" as a platform for offering key knowledge resources to those who can't afford larger, much more expensive options.
Read more about applications of the P3 platform


PARTEC Mobile HIV Testing
PARTEC CD4 & CD4% Counting
CyFlow® Counter
Portable / Mobile Flow Cytometer for
Routine CD4 (CD8, CD3) Counting
Net Price including 1000 free CD4 test:
EUR 16.850
Capacity: 250 Tests/Day
alignFree™ Technology
Cost per CD4 Test: EUR 1.75
CyFlow® SL_3
Portable / Mobile Flow Cytometer for
Routine CD4 and CD4% Counting
Net Price including 900 free tests:
EUR 20.850
Capacity: 250 Tests/Day
alignFree™ Technology
Cost per CD4 Test : EUR 1.75
Cost per CD4% Test : EUR 2.50
FLOW CYTOMETRY

Trypanosomiasis

- Tsetse fly (Bantu Name) *Glossina morsitans*
- *Trypanosoma brucei*



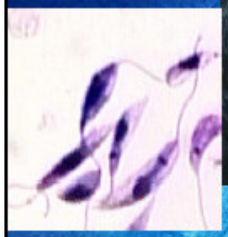
Rogers, DJ & S. Randolph. "Monitoring Trypanosomiasis in Space & Time." Parasitology. 1993; 351:739-741.

Schistosomiasis

- *Biomphylaria pfeifferi, B. tenagophila, B. glabrata, B. straminea & Bulinus truncatus*
- *Schistosoma mansoni*

Leishmaniasis

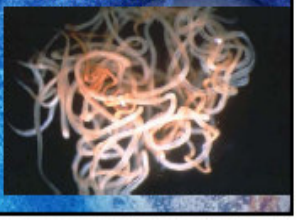
- Phlebotomus paptasi>>>
- Leishmania



Onchocerciasis

- Merck & Co. have donated Ivermectin, since Oct.'87 to treat onchocerciasis (150 mg/kg single dose) for microfilaria. Alternative: diethylcarbamazine (DEC) & Suramin (macrofilia)
- Temephos & clorphoxim insecticides resistance
- Adult worms life expectancy: 10-15 years

Onchocerca volvulus

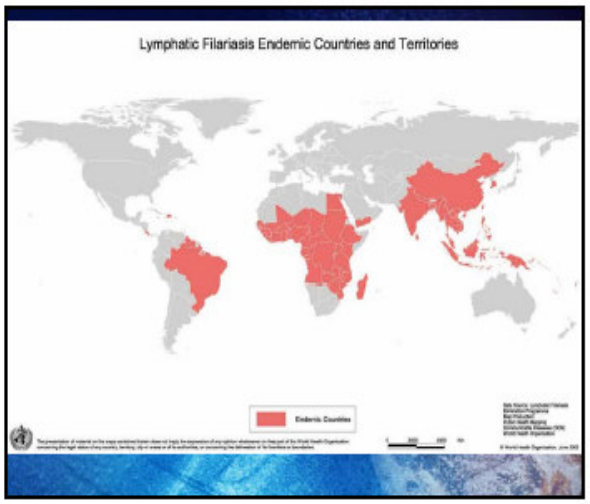


River Blindness

- 27 species of onchocerca affecting animals other than humans (Alfons Renz)

Elephantiasis (Lymphatic Filariasis, Lymphedema, *Wuchereria bancrofti* Infection, *Brugia malayi* Infection, *Brugia timori* Infection, *Loa loa* Infection

Elephantiasis is a parasitic disease which is transmitted from human to human by mosquito Aedes aegypti and other vector bites. The parasite tends to lodge in and block the lymph nodes that drain into the lower extremities, producing massive enlargement and deformity of the legs and genitalia

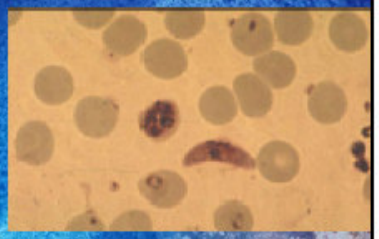


Heartwater (Cowdriosis)

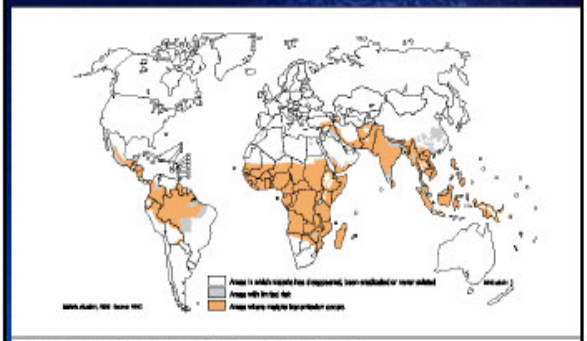
- *Cowdria ruminantium* transmitted by ticks: *Amblyomma*
- *Symptoms: fever,* hydropericardium, edema of lungs high mortality

Plasmodium Falciparum: Female Anopheles Mosquito

Above: Anopheles mosquito in characteristic biting and resting



Malaria

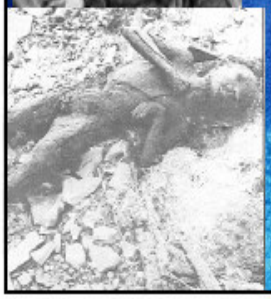


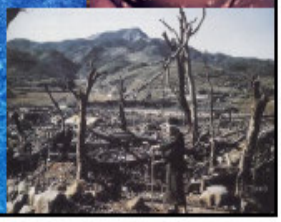
Above: World malaria situation. Malaria is endemic to tropical and subtropical regions.

Malaria

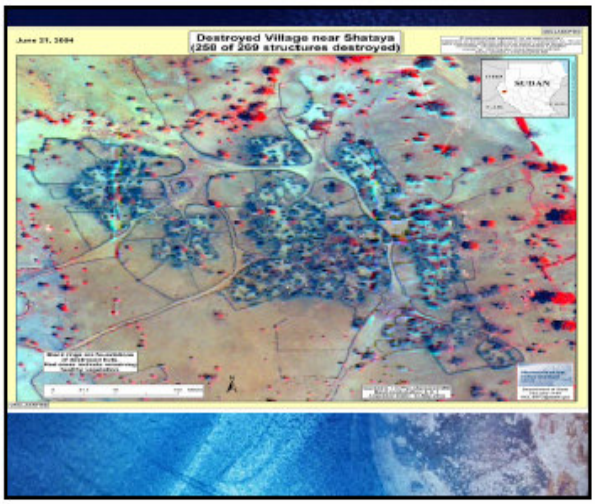
A child with malaria. Malaria kills an African child every 30 seconds.

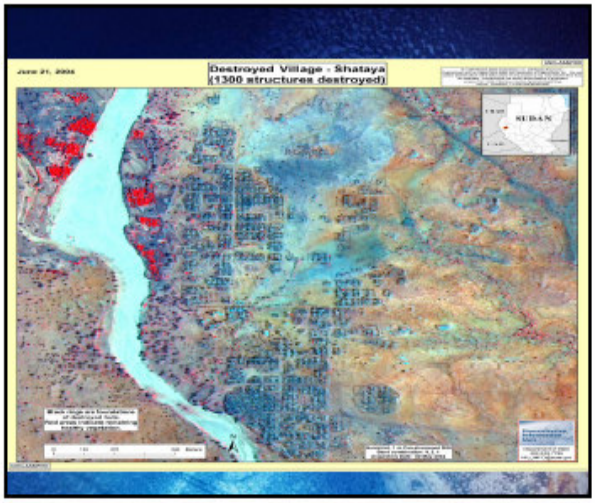
Nagasaki & Radiation Burns





Darfur Region, Sudan





Toward of Coalition of US University Groundstations

- Purdue University-Purdue Terrestrial Observatory & Lab for Applications of remote Sensing (LARS)
- University of Wisconsin
- University of Miami Rosenstiel School of Marine Science
- Scripps Institute of Oceanography – Univ. of California San Diego
- University of Texas at Austin
- Louisiana State University
- Elizabeth City State University
- University of Puerto Rico at Mayaguez
- Rutgers University
- City University of New York
- University of Alaska Fairbanks

Distributed Groundstations

- National University of Singapore
- University of Redding – UK
- Satellite Facility – Johannesburg, South Africa

Toward a Coalition of Turkish Universities and Research Institutes for Environmental Monitoring

- Istanbul Technical University (ITU)
- Middle East Technical University (METU)
- Bogazici University
- University of Marmara
- Aeronautical & Space Technology Institute (ASTIN)
- Kondili Observatory
- Mugla University

NATO Current STUDIES & PROJECTS

- Advanced Cancer Risk Assessment (Phase II) (Pilots: Italy & USA)
- Air Pollution Modeling and its application (Portugal & Turkey)
- Clean Products and Processes (USA)
- Ecosystem Modeling of Coastal Lagoons (Turkey)
- Ecoterrorism (Italy & Russia)
- Environmental Management Systems in Military Sector (Netherlands)
- Food Chain Security (Turkey)
- Integrated Water Management (Italy & Belgium)
- Landscape Science For Environmental Assessment (USA & Germany)
- Management of Industrial and Toxic Wastes (Greece)
- Prevention and Remediation Issues (USA)
- Risk Assessment of Chernobyl Accident (Italy & USA)
- Sustainable Building for Military Infrastructure (Canada & Netherlands)

NATO CCMS: PREVIOUS STUDIES

- Assessment of Natural Hazards (Canada)
- Design of the Caspian Basin Observing System (Turkey)
- Effective Risk Response Strategies (UK,USA)
- Environmental Decision Making in Central Asia (USA)
- Environmental Education in the Armed Forces (Canada & Poland)
- Improvement of Weather Forecasts (Greece)
- Security of Narrow Waterways (Turkey)

NATO: Proposed New Pilot Study Options

- Grid for Early Warning & Disaster Mitigation
- Real-Time Network for Time-Critical Applications
- Real-Time Remote & Proximate Sensing for
  - .....Sustainable Development
  - .....Environmental Sustainability
  - .....Biogenic & Anthropogenic Disasters

Precursor Alliances

- AmericaView
- GEON
- NcN
- University Astronomy Observatories

Corona, Lanyard & Argon: Multi-Temporal Change Detection

Need for Moderate Resolution & High Resolution Data:

Presentations/Publications

- Gilbert L. Rochon, Joseph E. Quansah & Hildred Sarah Rochon. The Role of Technology in Facilitating a Coalition Between Conventional Medical Practitioners and Indigenous Healers in the Struggle Against HIV/AIDS in Africa. Invited Presentation at the *Global Summit on HIV/AIDS, Traditional Medicine and Indigenous Knowledge*. Accra, Ghana, March, 2006.
- Gilbert Rochon. "Remote Sensing for Epidemics, Epizootics and Zoonoses," Purdue University International Veterinary Medicine Seminar, Purdue University, Dept. of Veterinary Medicine. March 30, 2006.
- Gilbert Rochon. "Remote Sensing as a Tool for Disaster Mitigation and Emergency Response," Wabash Area Lifelong Learning Association (WALLA), West Lafayette, Indiana. March 29, 2006.
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EFFICIENT TECHNOLOGY FOR PRECIOUS METALS EXTRACTION FROM SECONDARY RAW MATERIALS

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[3]*Institute of Power Engineering and Automation, Uzbek Academy of Sciences, Tashkent, Uzbekistan,*
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Abstract

An efficient pollution-free technology for precious metals extraction from secondary raw materials is being developed with financial support from the Science and Technology Center in Ukraine (STCU). Today, precious metals represent not only the source of wealth but, as well, the important material for engineering, electronics and science. Currently, the quantity of secondary raw materials containing precious metals appears to be comparable with natural sources. The existing technologies for processing of raw materials aim at the extraction of precious metals from large quantities of homogeneous primary raw materials having a low content of the metals. Methods and equipment used for this are very expensive and cannot be used for processing of small amounts of raw materials. Processing of secondary raw materials on the existing large-scale industrial equipment results in big losses of precious metals, since the peculiarities of such materials are not taken into account. Besides, the cost of processing of secondary raw materials by standard industrial methods often exceeds the value of precious metals being extracted.

The offered technology, which comprises a low-cost automated refining system, is mainly directed towards extraction of precious metals, such as gold, metals of platinum group and silver, from secondary row materials usually containing up to 5% (wt/wt) of precious metals. Such materials are originated from utilization, recycling, repairing and modernization of several generations of electronic and communication equipment and computers. They comprise: (i) scrap from rolling, cladding and punching, e.g., printing nips, contact springs, and clinchers, (ii) two- and multi-layer parts covered by a thin layer of precious metals, (iii) parts conjoined with plastics, ceramics, glass and other components of so-called electronic scrap, e.g., scrap of electronic parts, such as resistors, capacitors, switches and relays, devices for microwave technology, reading devices, converters, chips, hybrid microelectronic circuits, connectors, transistors, printed circuits, parts of commutation systems, etc. The technology is based on the method of chemical leaching that transfers all the metal compounds into the liquid phase enabling the sequential highly-efficient selective extraction of gold, silver and metals of platinum group with minimum losses, regardless of raw material composition and structure. The technology is directed towards total elimination of emission of hazardous substances into environment by using the closed-cycle technological scheme.

The fulfilment of the given project will allow construction of low-cost industrial plants for economically sound extraction of precious metals from secondary raw materials. It could be beneficial for the companies engaged in reprocessing of electronic parts and also for companies manufacturing electronic devices and facing the problems of dealing with scrap and defective parts.

The Science & Technology Centre in Ukraine (STCU) is an intergovernmental organization that enhancing international cooperation and partnerships.

The STCU located in Kiev was established in 1993 by Canada, Sweden and the United States. The European Union joined in 1998.

The STCU finances projects, which convert military know-how of the scientists into peaceful civilian applications.

Since 1993, STCU has managed over 940 R&D projects, worth over 133 million dollars.

Main Objectives of Collaboration

- Help integrate scientists from Ukraine, Georgia, Uzbekistan and Azerbaijan into the international scientific community
- Foster self-sustaining civilian activities of Ukrainian, Georgian, Uzbek and Azeri former weapon scientists
- Familiarize foreign organizations with unique Ukrainian, Georgian, Uzbek and Azeri science and research
- Offer project advice and assistance

Project Participants from the former Soviet Republics

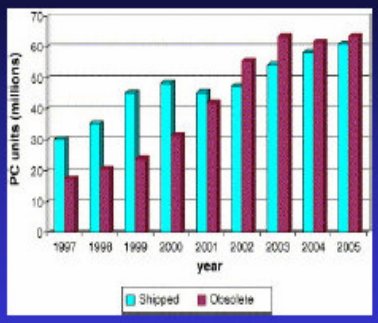
Research & Development Organizations:

- State Design Office "Yuzhnoye" (Dnepropetrovsk, Ukraine)
- Ukrainian State University of Chemistry and Technology (Dnepropetrovsk, Ukraine)
- Institute of Power Engineering and Automation of the Uzbek Academy of Sciences (Tashkent, Uzbekistan)

Industrial enterprises:

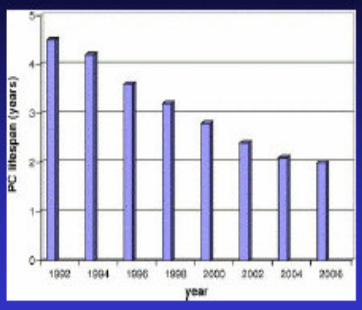
- Navoinsky-Almaliksky Mining and Metallurgical Combine
- Uzbek Corporation of Refractory and Heat-Resistant Metals
- Marzhanbulaksky Gold Mine
- Zerafshan-Newmont Corporation (gold mines)

Personal Computer (PC) Shipments and Obsolescence in the U.S.



From H.-Y. Kang, J.M. Schoenung. Resources, Conservation and Recycling 45 (2005) 368-400.

Personal Computer (PC) Average Lifespan in the U.S.



From H.-Y. Kang, J.M. Schoenung. Resources, Conservation and Recycling 45 (2005) 368-400.

An Explosion of Electronic Scrap

- Every year, 20 to 50 million tones of electrical and electronic equipment waste (e-waste) are generated worldwide
- More than 140,000 tones of computer equipment, phones, televisions, stereos, and small home appliances accumulate in Canadian landfills each year.
- 4 million PCs are discarded per year in China alone
- Only 14% of disused computers were recycled in 1999, and 125,000 tones of IT equipment are dumped in landfills in the UK alone, including two million working Pentium PCs
- E-waste already constitutes from 2 to 5% of the U.S. municipal solid waste stream and is growing rapidly
- About 15 million mobile phones are replaced in the UK each year. Mobiles contain precious metals such as platinum, palladium, gold, silver and copper. The majority of discarded mobile phones are deposited in landfill sites.

Composition of a Desktop Personal Computer*

Based on a typical desktop computer weighing ~60 lbs

Name	Content (% of total weight)	Weight of material in computer (lbs.)	Name	Content (% of total weight)	Weight of material in computer (lbs.)
Lead	6.2988	3.8	Titanium	0.0157	< 0.1
Aluminum	14.1723	8.5	Ruthenium	0.0016	< 0.1
Germanium	0.0016	< 0.1	Cobalt	0.0157	< 0.1
Gallium	0.0013	< 0.1	Palladium	0.0003	< 0.1
Iron	20.4712	12.3	Manganese	0.0315	< 0.1
Tin	1.0078	0.6	Silver	0.0190	< 0.1
Copper	6.9267	4.2	Antimony	0.0004	< 0.1
Barium	0.0315	< 0.1	Bismuth	0.0003	< 0.1
Nickel	0.8503	0.51	Chromium	0.0003	< 0.1
Zinc	2.2046	1.32	Cadmium	0.0004	< 0.1
Tantalum	0.0157	< 0.1	Selenium	0.0016	0.00096
Indium	0.0016	< 0.1	Niobium	0.0002	< 0.1
Vanadium	0.0002	< 0.1	Yttrium	0.0002	< 0.1
Beryllium	0.0157	< 0.1	Mercury	0.0022	< 0.1
Gold	0.0016	< 0.1	Arsenic	0.0013	< 0.1
Europium	0.0002	< 0.1	Silica	24.0063	15

*Table presented in: *Microelectronics and Computer Technology Corporation (MCC). 1996. Electronics Industry Environmental Roadmap. Austin, TX: MCC.*

In 1997-2004, over 315 million computers become obsolete in the USA alone

This adds up to:

- about 500,000 tones of lead: a typical computer monitor alone contains 2- 4 kilograms of lead
- 1,000 tones of cadmium: cadmium is listed as the 7th most dangerous substance on earth
- more than 200 tones of mercury: 22 % of the yearly world consumption of mercury is used in electrical and electronic equipment
- 2 million tones of plastic (mainly the most harmful PVC): on average, plastics make up more than 6 kilogram per computer
- significant amount of brominated flame-retardants: various scientific observations indicate that polybrominated diphenylethers can disrupt the endocrine system

Electronic Parts Containing Precious Metals

Capacitor & transistor production rejects. Their leads contain gold.

Ceramic substrates bear platinum, palladium & ruthenium.

Solder salvaged from PC board soldering operations. The solder contains gold, lead & tin.

Miscellaneous electronic scrap containing precious metals.

The gold plating on the pins.

Blanking scrap – gold on beryllium copper.

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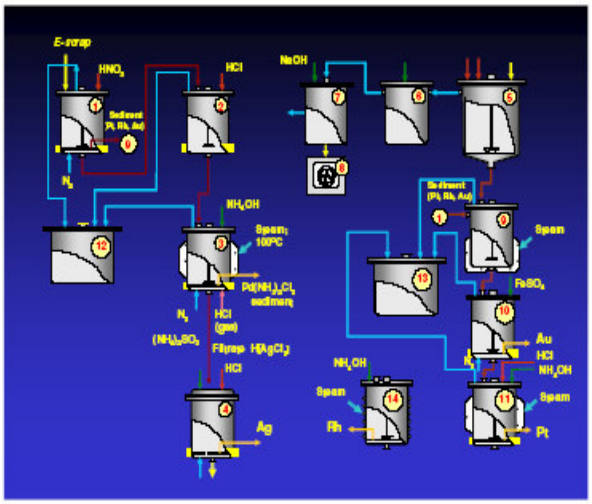
Disadvantages of Existing Technologies

- Designed for the extraction of precious metals from large quantities of homogeneous primary raw materials having a low content of the metals
- Methods and equipment utilized are very expensive and cannot be used for processing of small amounts of raw materials
- Processing of secondary raw materials on the existing large-scale industrial equipment leads to big losses of precious metals
- Routinely, the cost of extraction exceeds the value of precious metals being extracted



Preparation steps:

- Sorting the secondary raw material
- Printed board extraction
- Electronic components removal from the board
- Crushing and grinding to the required grain size
- Loading into reactor

Leaching and separation of the metals

(Ag, Pd, Cu, Pt, Rh, Au, Fe) + $HNO_{3(diluted)}$ → Ag^+, Pd^{2+}, Cu^{2+}, Fe^{2+} + (Pt, Ru, Au)

$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O$

$3Pd + 8HNO_3 = 3Pd(NO_3)_2 + 2NO + 4H_2O$

Ag^+, Pd^{2+}, Cu^{2+}, (Fe^{2+}) + $Fe_{(powder)}$ → Ag^o, Pd^o, Cu^o + (Fe^{2+})

"Aqua regia": $3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O$

(Ag, Pd, Cu) + "aqua regia" → Ag^+, Pd^{2+}, Cu^{2+}

Extraction of metals

Extraction of silver:

$AgNO_3 + 2HCl = H[AgCl_2]\downarrow + HNO_3$

$2H[AgCl_2]\downarrow + (NH_4)_2SO_3 + H_2O = \underline{2Ag} + 2NH_4Cl + + 2HCl + + H_2SO_4$

Extraction of palladium:

$3Pd + 8HNO_3 = 3Pd(NO_3)_2 + 2NO + 4H_2O$

$Pd(NH_3)_4Cl_2] + (HCl) = [Pd(NH_3)_2Cl_2] + 2NH_3$

$[Pd(NH_3)2Cl_2] = \underline{Pd} + 2NH_3 + Cl_2$

Leaching of gold, platinum, and rhodium by "aqua regia"

$Au + HNO_{3(conc.)} + 4HCl_{(conc.)} = H[AuCl_4] + NO + 2H_2O$

$3Pt + 4HNO_{3(conc.)} + 18HCl_{(conc.)} = 3H_2[PtCl_6] + 4NO + 8H_2O$

$3Rh + 4HNO_{3(conc.)} + 18HCl_{(conc.)} = 3H_2[RhCl_6] + 4NO + 8H_2O$

Extraction of gold:

$H[AuCl_4] + 3FeSO_{4\,(15\%)} = \underline{Au} + Fe_2(SO4)_3 + FeCl_3 + HCl$

Extraction of platinum:

$H_2[PtCl_6] + 2NH_4Cl = (NH_4)_2PtCl_6 + 2HCl$

$3(NH_4)_2PtCl_6 = \underline{3Pt} + 2N_2 + 2NH_4Cl + 16HCl$

Extraction of rhodium:

$3H_2[RhCl_6] + 3FeSO_4 + 3HCl = 3H_3[RhCl_6] + Fe_2(SO_4)_3 + FeCl_3$

$H_3[RhCl_6] + 5NH_4OH = [Rh(NH_3)_5Cl]Cl_2 + 3HCl + 5H_2O$

$2[Rh(NH_3)_5Cl]Cl_2 = \underline{2Rh} + 10NH_3 + 3Cl_2$

Utilizing of By-products

Obtaining nitrogen-containing fertilizers:

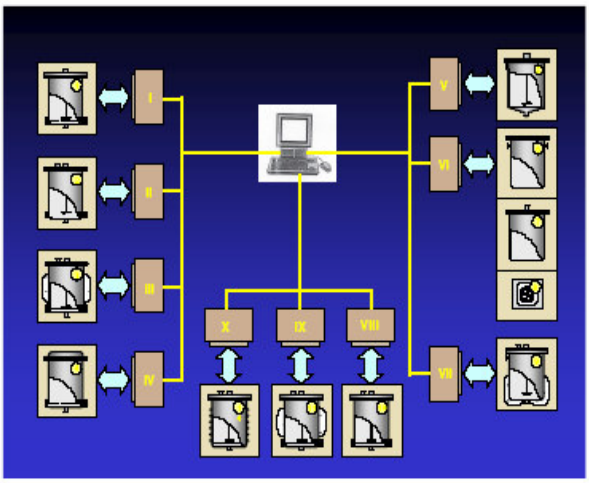
NO_X + (KOH or NH_4OH) → Nitrogen-containing fertilizers

$SO_X \rightarrow (NH_4)_2SO_4$

NH_3 → Nitrogen-containing fertilizers

Main Advantages of Proposed Technology

- A possibility to process relatively small volumes of raw materials, starting from 100 g of pure gold
- Flexibility of design allowing reorganization of the process in accordance of type of raw material
- Small capital cost
- Mobility: the possibility of quick assembly and launching of the unit at new location
- Economical efficiency: given technology allows purchasing of the raw materials at 50-70% of the gold market price



Automation of the Process

Manual Operations:

- *Grading*
- *Extraction of the printed boards*

Fully-automated operations:

- *Removal of electronic parts*
- *Crushing to the required grain size*
- *Loading and unloading of reactors*
- *Filtration and rinsing*
- *All chemical reaction*

RED MUD – A POTENTIAL SORBENT FOR REMOVAL OF HEAVY METAL CATIONS

Miroslava Vaclavikova

Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, Kosice, Slovakia

Abstract

The presence of metal ions in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end–products. The metals of most immediate concern are Cr, Mn, Fe, Zn and Cd. These metals are widely distributed in materials, which make up the earth's surface. Due to their toxicity, the maximum concentration levels for drinking and surface waters have been set. Increasingly stringent European legislation on the purity of drinking waters has created a growing interest in the development of conventional treatment processes. Various methods of wastewater treatment were examined and adsorption proved as one of the most promising techniques. The aim of this research has been to undertake a study to assess the potential of red mud as a sorbent for the removal of toxic metal ions – such as cadmium, zinc, copper and lead. The toxicity and colloidal nature of the red mud particles as well as the relatively large quantities generated create a serious pollution hazard and needs a "search out" for an improved disposal technique.

The red mud (RM) is an insoluble fine–grained residue of alumina production from the Bayer process for extracting alumina from bauxite, where the ground ore is treated with hot concentrated base. Roughly 1.0–1.5 tones of red mud residue are produced for each tone of alumina and hence, millions of tones of caustic red mud must be disposed of annually worldwide. The disposal of red mud is associated with space/real estate near industry and cost of disposal and pollution, which are now crucial factors. The red mud from aluminium oxide production at Ziar nad Hronom, Slovakia represents significant hazard to the environment too. There is about 10 million tons of waste dumped near processing plant. The waste dump occupies about 40 hectares. Therefore, the exploitations of these by–products in other areas are of growing importance for basic industries and also for the environment. The major constituents of red mud are Fe_2O_3, TiO_2, Al_2O_3, CaO, SiO_2 and Na_2O.
Red mud, due to its high aluminium, iron and calcium content, has been suggested as an inexpensive adsorbent for the removal of toxic metals. Cadmium, lead, copper and zinc were selected as test cations for the investigation of the sorption properties of red mud in this study. Cadmium and lead are elements occupying high toxicity positions in the EPA tables. On the other hand, copper and zinc are elements taking part in many biological processes but considered as toxic and hazardous to human health at elevated concentrations. The TCLP test results indicate that the red mud is generally an environmentally friendly material that could be applied to efficiently treat wastewaters. Red mud, a solid byproduct of the alumina production industry, was found to be a sorbent able to remove cadmium, zinc, lead and copper from model aqueous solutions.

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Red Mud – A Potential Sorbent for Removal of Heavy Metal Cations

Miroslava Vaclavikova

Red Mud

- Insoluble fine-grained residue of alumina production from the Bayer process for extracting alumina from bauxite;
- roughly 1.0–1.5 tonnes of red mud residue are produced for each tone of alumina ⟶ hence, millions of tonnes of caustic red mud must be disposed worldwide annually.
- It has been accumulated at a rate of 30 million tonnes per annum throughout the world

Significant hazard to the environment

- about 10 million tonnes of waste dumped near the processing plant

Growing importance

EXPLOITATION = APPLICATION

Research Overview

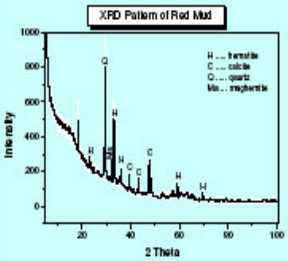
- **Material study**
  - chemical composition
  - mineral composition
  - grain size
  - surface area – BET method
  - magnetic susceptibility
  - pH measurements
- **Model sorption study**
  - batch–type experiments
    Cd, Zn, Pb and Cu.

Material Study ... Results

Chemical composition

Element	Content [%]
SiO_2	13.35
Fe_{total}	25.34
Fe^{2+}	0.56
Fe^{3+}	24.78
Ca	1.066
Mg	0.35
Al	4.43
Cr	0.039
Pb	0.011
Zn	0.014
Mn	0.42
Na	6.88

Mineral composition

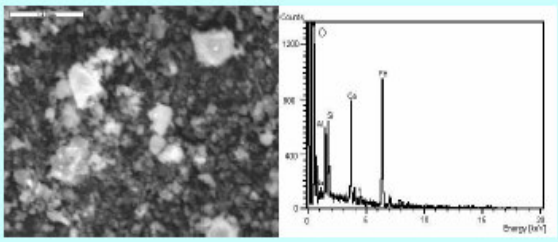


Diffractometer: Philips X'Pert Pro

Material Study ... Results

SEM Micrograph

(JEOL JSM 840-A equipped with a Link ISIS 300 EDS)



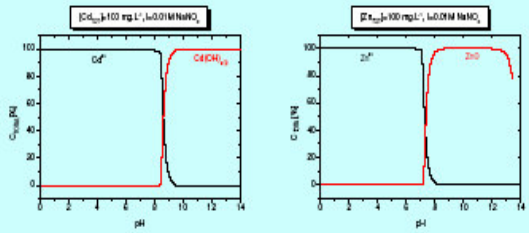
fine–grained powder (90% -22μm)

$S_A = 18.38\ m^2.g^{-1}$

Sorption Study

Thermodynamic Equilibrium Diagrams

(MINEQL PLUS)



Cd ... soluble ... pH≤8,3

pH_{prec}= 8,4 ..... $Cd(OH)_{2(s)}$

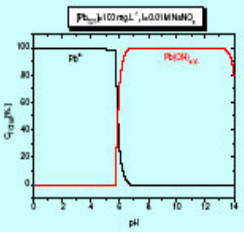
Zn ... soluble ... pH≤7,3

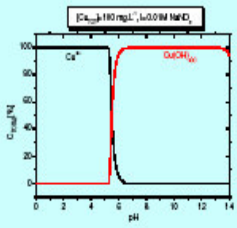
pH_{prec}= 7,4 ..... $ZnO_{(s)}$

Sorption Study

Thermodynamic Equilibrium Diagrams

(MINEQL PLUS)





Pb ... soluble ... pH≤5.8

pH_{prec}= 5.9 ..... $Pb(OH)_{2(s)}$

Cu ... soluble ... pH≤5.4

pH_{prec}= 5.5 ..... $Cu(OH)_{2(s)}$

Sorption Experiments

Sorption conditions

- *Sorbent concentration ..... 2 g.L⁻¹*
- *Initial Me^{2+} concentration ... 20 – 400 mg.L⁻¹*
- *Adsorption time ..... 24 hr.*
- *Temperature (const.) ..... 25°C*
- *Ionic strength ..... I=0,01*

✓ *S/L separation .... Filtration*

✓ *Determination of concentration of heavy metals ... AAS*

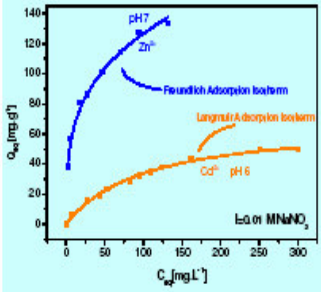
Sorption Experiments

$$Q_{eq} = \frac{C_{init} - C_{eq}}{C_S}$$

C_{init}[mg.L⁻¹] ... initial concentration

C_{eq}[mg.L⁻¹] ... equilibrium concentration

C_S [g.L⁻¹] ..... sorbent concentration



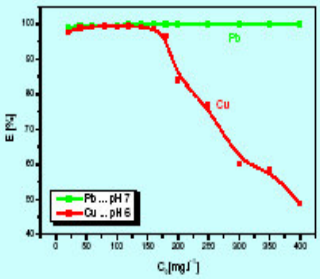
Adsorption Parameters			
Cd Langmuir	Q_{max}	K	R^2
	68.18	0.009	0.99
Zn Freundlich	K	b	R^2
	33.05	0.29	0.99

Sorption Experiments

pH increases over pH_{prec}

Precipitation

$$E = \frac{C_0 - C_{eq}}{C_0} . 100[\%]$$



Conclusion

✓ *the red mud was found to be an efficient sorbent for the removal of cadmium and zinc bivalent cations from water solutions with the sorption capacity of 68 mg/g for cadmium at pH 6 and 133 mg/g for zinc at pH 7 ;*

✓ *Almost 100% of lead was removed due to precipitation*

✓ *it is believed that mentioned material can be successfully used for the treatment of wastewaters containing Cd^{2+} and Zn^{2+}.*

Some Memories from 2006 Istanbul Meeting

Prof. Dr. Fatoş Y. Vural, Vice Rector of METU, delivering her opening

Dr. Subhas Sikdar, Director of the Pilot Study, delivering his opening speech

Delegates during the meeting

Delegates during the meeting

Boat tour on Bosphourus

Beylerbeyi Palace on Bosphourus

Technical visit to the Marmara Research Center (May 9, 2006)

Technical visit to the FORD automotive industry (May 9, 2006)

Technical visit to the FORD automotive industry (May 9, 2006)

Technical visit to the GOODYEAR tire manufacturing company (May 9, 2006)