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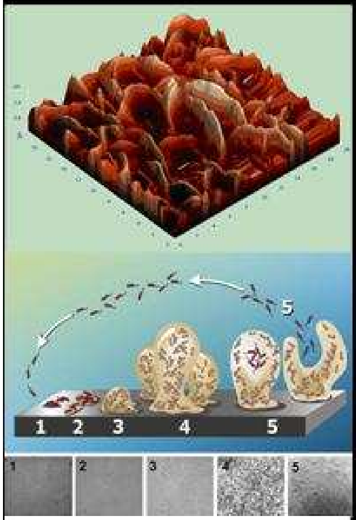

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Nanoscale Electrochemical and Bioprocesses (Corrosion) at Solid-aqueous Interfaces of Industrial Materials

Editura Alma Print

Dunarea de Jos University of Galati - Romania
Competences Center: Interfaces-Tribocorrosion and
Electrochemical Systems (CC-ITES)
Babeş-Bolyai University Cluj – Napoca - Romania
Raluca Ripan Chemistry Research Institute

COST D33

Nanoscale Electrochemical and Bioprocesses (Corrosion) at Solid-aqueous Interfaces of Industrial Materials

Final WORKSHOP

May 13th 2009 – May 15th 2009

Cluj - Napoca , ROMANIA

Editors: Prof. Dr. Lidia BENEA, Prof. Dr. Geta CÂRÂC

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Plenary lectures

WG1
Development, adaptation and coupling of surface science methods for an improved analysis of the chemical processes occurring at the interfaces between materials and micro-organisms

WG2
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WG3
Understanding of the elementary steps leading to biocorrosion, biofouling, biofilms, bioleaching etc. in order to inhibit or improve the respective processes: Applications in practice

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Posters

COST D33 - CHEMISTRY

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FINAL PROGRAMME

Tuesday: 12 of May 2009	
	Arrivals
17h00 - 19h00	Registration
19h00	**Welcome party**
Wednesday: 13 of May 2009	
9h00 9h30	**Welcome – Opening** **-Chair. Prof. Wolfgang SAND** **-Prof. Luminita SILAGHI DUMITRESCU: Babes Bolyai University Vice – President** **-City Administration** **-COST Official**
9h30-9h45	**Introduction to COST D33 & Presentation of WGs** **Prof. Wolfgang SAND – Chairman of COST D33 Action** *University of Duisburg Essen, Germany*
Chairman - Prof. Wolfgang SAND	
9h50-10h40	**Plenary Lecture** **Prof. Brenda J. LITTLE** **RECENT DEVELOPMENTS IN THE STUDY OF MICROBIOLOGICALLY INFLUENCED CORROSION** Brenda J. Little, Richard I. Ray and Jason S. Lee *Naval Research Laboratory, Stennis Space Center, MS 39525 USA*
10h40-11h00	**Coffee Break**
Chairman – Dr. Gabriele FERRARI	
11h00-11h30	**Prof. Philippe MARCUS (WG1)** **Adsorption of fibronectin on model surfaces of biomaterials and effect on cellular adhesion and proliferation.** Vincent Payet, Tonia Dini, Isabelle Frateur, Anouk Galtayries, Pascale Vigneron, Marie Danielle NAGEL, Philippe Marcus *Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR7045), Ecole Nationale Supérieure de Chimie de Paris – France.*
11h30-12h00	**Prof. Bernard TRIBOLLET (WG1)** **Electroacoustic miniaturized DNA-biosensor** Bernard Tribollet and Jean Gamby *Laboratoire Interfaces et Systèmes Electrochimiques, UPR 15 du CNRS, Université Pierre et Marie Curie, Paris – France*
12h00-12h30	**Dr. Georg PAPASTAVROU (WG1)** **Probing polysaccharide adhesion by AFM** S. Tumbiolo, G. Papastavrou *University of Geneva, Sciences II, Switzerland*
12h30-13h00	**Invited speaker of WG1: Dr. José L. TOCA-HERRERA** **Proteins and Cells at interfaces investigated by QCM-D and AFM** *E. Eleta, S. Moreno-Flores, M. dM. Vivanco, R. Georgieva, H. Baumler, D. Pum, U. B. Sleytr, J. L. Toca-*

	Herrera *Biosurfaces Unit, CIC BiomaGUNE, San Sebastián, Spain*
13h00- 13h30	**PhD. Alina CIUBOTARIU (WG1)** **Combined AFM and EFM for visualization of sulphate reducing bacteria on thermosetting resin / Zn composite coatings** Alina Ciubotariu, Lidia Benea, Wolfgang Sand *Dunarea de Jos, University of Galati, CC-ITES, Romania*
13h30- 15h00	**Lunch**
15h00- 16h00	**I Committee (MC) Meeting** -Members of MC & WG`s Leaders. -COST Officials
15h00- 16h00	**Tour & Scientific Visit** Workshop participants (non MC members)
Chairman – Prof. Glyn MORTON	
16h00- 16h30	**Prof. Luca OTTAVIANO (WG1)** **Nanopatterned XIL substrates for nano-bio applications** L. Ottaviano, P. Zuppella, S. Prezioso, P. De Marco, S. Di Bucchianico, M.F. Giardi, D. Botti, A. Reale, and S. Santucci *STN lab Department of Physics & Deparment of Biology University of L'Aquila, Italy*
16h30- 17h00	**Dr. Almira RAMANAVICIENE (WG2)** **Electrochemical and optical methods in glucose oxidase distribution and activity research** Almira Ramanaviciene, Asta Kausaite-Minkstimiene[a], Arunas Ramanavicius *Institute of Immunology of Vilnius University, Lithuania*
17h00- 17h30	**Dr. Paula COJOCARU (WG2)** **New innovative composite materials obtained by electrodeposition with high biocompatibility** *Politecnico di Milano Italy*
17h30- 17h50	**Cofee Break**
Chairman – Dr. Georg PAPASTAVROU	
17h50- 18h20	**Prof. Paul ROUXHET (WG2)** **XPS analysis of stainless steel at early stages of biofilm formation: from elements to chemical functions and molecular compounds.** Paul G. Rouxhet, Jessem Landoulsi *Unité de chimie des interfaces, Université catholique de Louvain, Louvain-la-Neuve, Belgium.*
18h20- 18h50	**PhD. Andrzej KUKLINSKI (WG2)** **Application of extracellular polymeric substances for preventing microbially influenced corrosion** Andrzej Kuklinski, Reinhard Stadler, Wolfram Fürbeth, Wolfgang Sand *University Duisburg-Essen, Biofilm Centre / Aquatic Biotechnology, Germany*
18h50- 19h20	**Prof. Geta CARAC (WG2)** **Electrochemical and AFM study of the cells effect on stainless steel and Ni-composite coatings**

	Geta Cârâc, Maricica Stoica, A. Ramanaviciene and A. Ramanavicius *Dunarea de Jos University of Galati, Romania*
20h00	**Dinner**
Thursday: 14 of May 2009	
Chairman – Prof. Lidia BENEA	
9h00-9h50	**Plenary Lecture** **Prof. Ji-Dong GU** **OXIDATION OF AS(III) IN THE PRESENCE OF FE(II) BY ON Β-MNO$_2$ UNDER ACIDIC CONDITIONS** Xu Han and Ji-Dong Gu *Laboratory of Environmental Microbiology and Toxicology, School of Biological Science,* *The University of Hong Kong, Hong Kong SAR, China*
9h50-10h50 9h50-10h20	**Dr. Judith TELEGDI (WG2)** **How can nanolayers control the microbial adhesion and corrosion?** J. Telegdi, L. Romanszki, E. Kalman *Department of Surface Modification and Nanostructures, Institute of Surface Science and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, Hungary*
10h20-10h50	**Prof. Arunas RAMANAVICIUS (WG2)** **Application of some issues related to biocorrosion in biofuel cells** Arunas Ramanavicius, Almira Ramanaviciene *Vilnius University, Center of Nanotechnology and Materials Science, Lithuania*
10h50-11h10	**Coffee Break**
Chairman – Prof. Geta CÂRÂC	
11h10-11h40	**Dr. Gabriele FERRARI (WG2&WG3)** **Exopolysacharide eps180 as anti-corrosive additives for coatings** G.M.Ferrari *TNO – Netherlands Organisation for Applied Scientific Research, Den Helder, Netherlands*
11h40-12h10	**Prof. Glyn MORTON (WG3)** **An account of the antimicrobial activity of a helical peptide and an evaluation of its use as a surface coating on fabric against bacterial contamination** Sarah Dennison, Glyn Morton *University of Central Lancashire Preston UK*
12h10-12h40	**Dr. Ana M. GARCÍA (WG3)** **Bioremediation of radioactive water in nuclear power plants** Ana M. García, Constantino Ruibal, Diego A. Moreno *Universidad Politécnica de Madrid, Dep. de Ingeniería y Ciencia de los Materiales, Escuela Técnica Superior de Ingenieros Industriales, Spain*

12h40- 13h10	**Prof. Lisbeth RISCHEL HILBERT (WG3)** **Bacterial interactions with Ag-bearing surfaces: Ag-Pd coating and Ag-bearing stainless steel** Lisbeth Rischel Hilbert, Wen-Chi Chiang, Per Møller *FORCE Technology, Denmark*
13h10- 13h30	**Dr. Cristina PREJMEREAN (WG2&WG3)** **Study of dental tissues/resin-based materials interface** C. Prejmerean, M. Moldovan, M. Trif, L. Silaghi-Dumitrescu, G. Furtos, D. Prodan, C.Sarosi, S.Boboia *Babes Bolyai University, Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*
13h30- 15h00	**Lunch**
Chairman of Posters Session – Dr. Almira RAMANAVICIENE	
15h00- 16h00	**OUTLOOK SESSION – POSTERS** **All participants**
Chairman – Prof. Lisbeth RISCHEL HILBERT	
16h00- 16h30	**Dr. Carmen SANJOSE (WG3)** **Biofilm in microtiter plates. What do we measure?** Carmen SanJose, B. Orgaz, M. Martinez and J. Villanueva *Dpt. Of Nutrition, Food Science and Technology, Veterinary Faculty, Complutense University of Madrid, Spain*
16h30- 17h00	**Dr. Françoise FEUGEAS (WG3)** **EPS180 Properties in concrete as anti-corrosion and anti-microbial reagent: a challenge?** Sébastien Roux, Mohamed Miqyas, Gabriele Ferrari, Françoise Feugeas *INSA de Strasbourg, Laboratoire de Génie de la Conception EA 3938, Strasbourg, France*
17h00- 17h30	**PhD. Fabio MUSCOLINO (WG2&WG3)** **Comparison of the electrochemical behaviour of stainless steels in abiotic and biotic seawater** F. Muscolino, P.Cojocaru, L. Magagnin, P.L. Cavallotti *Politecnico di Milano, via Mancinelli, 7 20131 Milan, Italy.*
17h30- 17h40	**Coffee Break**
Chairman – Prof. Bernard TRIBOLLET	
17h40- 18h10	**Prof. Lidia BENEA (WG1&WG3)** **Materials characteristics influencing biofilm formation and growth** Lidia Benea, Alina Ciubotariu, Wolgang Sand, Bernard Tribollet *Dunarea de Jos University of Galati, Competences Center Interfaces –Tribocorrosion and Electrochemical Systems (CC-ITES), 47 Domneasca St., 800008 Galati, Romania*
18h10- 18h40	**Prof. Dr. Magda LAKATOS-VARSÁNYI (WG2&WG3)** **Electrochemical studies of the titanium implants in chloride solution** Authors: M. Lakatos-Varsányi, C. Suba, A. Mikó, G. Szabó[2], T. Pozman, M. Furkó *Bay Zoltán Foundation, Institute for Materials Science and Technology, Budapest, Hungary*
19h00	**Conference Dinner**

Friday: 15 May 2009	
Chairman –Prof. Arunas RAMANAVICIUS	
9h30-9h50	**Plenary Lecture** **Prof. Pietro Luigi CAVALLOTTI** **Electrodeposition of nanostructured surfaces** *Politecnico di Milano, Italy*
9h50-10h20	**Dr. Anne HEYER (WG3)** **Microbially influenced corrosion in shiptank environments** A. Heyer, F. D'Souza, G. Ferrari, J.M.C. Mol and J.H.W. de Wit *M2i Materials Innovation Institute, Mekelweg 2 2628 CD Delft, The Netherlands*
10h20-10h50	**Dr. Gerhard F. REMMERS (WG2&WG3)** **COST D33 – Pro's and Con's, an impression of experiences from industry** *AkzoNobel Research, Development & Innovation – Arnhem – The Netherlands*
10h50-11h10	**Coffee Break**
Chairman – Prof. Philippe MARCUS	
11h10-11h25	**COST D33 – WG1 Summary** **Prof. Lidia BENEA** *Dunarea de Jos University of Galati – CC-ITES, Romania*
11h25-11h40	**COST D33 – WG2 Summary** **Prof. Geta CÂRÂC** *Dunarea de Jos University of Galati, Romania*
11h40-11h55	**COST D33 – WG3 Summary** **Dr. Gabriele FERRARI** *TNO Industry, Netherlands*
11h55-12h10	**COST D33 – STSM Report** **Prof. Bernard TRIBOLLET** *Laboratoire Interfaces et Systèmes Electrochimiques UPR 15 du CNRS, France*
12h10-12h30	**External Expert Evaluation** **Prof. Brenda J. LITTLE**
12h30-12h50	**External Expert Evaluation** **Prof. Ji-Dong GU**
12h50-13h10	**COST DC Rapporteur** **Prof. Vasile PARVULESCU**
13h10-13h30	**Closing Remarks** **Prof. Wolfgang SAND**
13h30-15h00	**Lunch**
15h00 -	Round Table. Social Program. Excursion
Saturday: May 16, 2009 Touristic Places Visit. Departures	

POSTERS

Presenting Author/Affiliation		Title /Authors
P.1.	**Dr. Sarah DENNISON** *University of Central Lancashire Preston UK*	**Characterization of an antimicrobial peptide aurein 2.5 with bacterial membranes** Sarah R Dennison, Leslie H G Morton, Andrea J Shorrocks, Frederick Harris and David A Phoenix
P.2.	**PhD. Remus MIHAILA** *Dunarea de Jos University of Galati, CC-ITES, Metallurgy and Materials Science, Galati, Romania*	**ZrO_2/Co new functional bio composite coatings** Remus Mihaila, Lidia Benea, Marilena Mardare, Paula Cojocaru
P.3.	**Dr Natalija GERMAN** *Vilnius University, Lithuania*	**Catalytic effect of glucose oxidase and gold nanoparticles on biocorrosion processes** Natalija German, Arturas Suchodolskis, Almira Ramanaviciene, Arunas Ramanavicius, Jaroslav Voronovic
P.4.	**PhD. Marilena MARDARE** *Dunarea de Jos University of Galati, Competences Center Interfaces – Tribocorrosion and Electrochemical Systems (CC-ITES), Galati, Romania*	**Influence of UHMWPE/Co composite coatings on biofilm formation, biocompatibility and degradation** Marilena Mardare, Lidia Benea, Paula Cojocaru
P.5.	**PhD. Simona-Florentina SORCARU** *Dunarea de Jos University of Galati, Competences Center Interfaces – Tribocorrosion and Electrochemical Systems (CC-ITES), Galati, Romania*	**Nano-Composite Coatings – Functional Surfaces in Decreasing the Bacterial Adhesion – Surface Study** Lidia Benea, Simona-Florentina Sorcaru, Pierre Ponthiaux
P.6.	**PhD. Alina CANTARAGIU** *Dunarea de Jos University of Galati, Department of Physics, Romania*	**Study of TiO_2/Hydroxyapatite Stainless Steel – nanocomposite coatings at the cells adhesion** Alina Cantaragiu**,** Geta Cârâc, Paula Cojocaru
P.7.	**PhD. Maricica STOICA** *Dunarea de Jos University of Galati, Faculty of Engineering Food, Romania*	**Electrochemical behaviour of cells adhesion on the Stainless Steel 304 in the disinfectant medium** M. Stoica, G. Cârâc, A. Ramanaviciene and A. Ramanavicius
P.8.	**Dr. Asta Kausaite-MINKSTIMIENE** *Centre of nanotechnology and material science – NanoTechnas, Vilnius University, Lithuania*	**From biocorrosion to enzymatic biofuel cells powered by ethanol and glucose** A. Kausaite-Minkstimiene, A. Ramanaviciene, A. Ramanavicius
P.9.	**Dr. Denny THIEMIG** *Department of Physical Chemistry Dresden University of Technology, Dresden, Germany*	**Electrocodeposition of ZnFe/Hydroxyapatite nanocomposites** Denny Thiemig, Alina Cantaragiu, Geta Cârâc, Andreas Bund
P.10.	**Dr. Tatjana ROMASKEVIC** *Institute of Immunology of Vilnius Department of Polymer Chemistry, Vilnius University, Lithuania*	**Polyurethane-gold nanoparticles bioconjugates with enhanced biostability** Tatjana Romaskevic, Saulute Budriene, Almira Ramanaviciene
P.11.	**Prof. Anisoara CIOCAN** *Dunarea de Jos University of Galati, Faculty of Metallurgy and Materials Science, Romania*	**Aluminium nickel alloys cladding on steel support for hard mechanical requirements used for the bearings offshore drilling equipments** Anisoara Ciocan, Tamara Radu, Florentina Potecasu

P.12.	**PhD. Marcela TRIF** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**Metal Oxide-Hydroxyapatite Biphasic Materials Studied by SEM Microscopy.** M. Trif **,** M. Moldovan, D. Prodan, C. Prejmerean, C. Sarosi , L. Silaghi-Dumitrescu, M. Rusu, Cornel Trisca Rusu
P.13.	**Doina PRODAN** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**SEM Study for Interaction Between Biocomposites and Co Alloys** D. Prodan, M. Moldovan**,** I. Roman, M. Trif, C.Prejmerean, O.Musat, G. Ioncea, L. Silaghi Dumitrescu
P.14.	**Dr. Gabriel FURTOS** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**Radiopacity of flowable resin composites compared with human tooth structure.** G. Furtos, B. Baldea, D. Bratu, C. Prejmerean, L. Silaghi-Dumitrescu
P.15.	**PhD. Laura SILAGHI-DUMITRESCU** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**The Effect of Experimental Bleaching Agent on Dental Composites** L. Silaghi-Dumitrescu, M. Moldovan, C. Prejmerean, G. Furtos, D. Prodan, D. Dudea, C. Sarosi, S. Boboia
P.16.	**Stud. Stanca BOBOIA** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**Biological tests for new experimental nanocomposites** **S. Boboia**, M. Moldovan, C. Sarosi, C. Prejmerean, O. Musat, M. Trif, D. Prodan, L. Silaghi Dumitrescu, G. Furtos
P.17.	**PhD. Codruta SAROSI** *Babes Bolyai University – Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania*	**Degree of Conversion of Some New Experimental Dental Adhesives** C. Sarosi, M. Moldovan, O. Fodor, C. Prejmerean, G. Popescu, M. Trif, M. Rusu, S. Boboia
P18	**Guenter SCHMITT** *Institut für Instandhaltung und Korrosionsschutztechnik gGmbH, Iserlohn, Germany*	**Guenter SCHMITT (WG1&WG3)** **MIC in Stainless Steel Plumbing Systems for Drinking Water** Guenter Schmitt, Hubertus Schlerkmann, Wolfgang Sand, H. Klemp *Institut für Instandhaltung und Korrosionsschutztechnik gGmbH, Iserlohn, Germany*

Plenary lectures

RECENT DEVELOPMENTS IN THE STUDY OF MICROBIOLOGICALLY INFLUENCED CORROSION

Brenda J. Little, **Richard I. Ray and Jason S. Lee**

Naval Research Laboratory, Stennis Space Center, MS 39525
E-mail: blittle@nrlssc.navy.mil

Many of the recent developments in our understanding of microbiologically influenced corrosion (MIC) can be attributed to improved methods for identifying microorganisms. Liquid culture techniques, the standard method for identifying and enumerating specific types of bacteria, underestimate the complexity of microbial communities. Several investigators have demonstrated dramatic changes in microbial populations after samples were introduced into liquid culture media. Some bacteria present in small amounts in the original waters were enriched in the culture process. For example, using culture techniques sulfate-reducing bacteria (SRB) appear to dominate the microflora in many industrial settings. However, using culture-independent genetic techniques Zhu (2003) found that methanogens were more abundant in most pipeline samples than denitrifying bacteria and that SRB were the least abundant bacteria. Furthermore causative microorganisms are from all three main branches of evolutionary descent, i.e., Bacteria, Archaea and Eukaryota, and it is now recognized that not all sulfide-producing microorganisms are bacteria. The list of microorganisms involved in MIC and the resulting mechanisms that cause MIC is continuously growing, and now includes microbially influenced reactions that were not previously linked to MIC, e.g., iodide oxidation and methane production.

Despite the improved techniques for identifying naturally occurring microorganisms there are inherent difficulties in establishing relationships between specific numbers and types of microorganisms and MIC. Consequently there has been a shift away from attempting to quantify bacterial types to evaluating the chemistry and electrochemistry that result from the activities of microorganisms. The approaches to two case studies will be presented: 1) production of carbon dioxide and acetate by fermentative, acetogenic and SRB residing in pipeline facilities and 2) bacteriogenic iron oxide (BIOS) production by iron-oxidizing bacteria in a fresh water lake. The exacerbation of carbon dioxide corrosion of carbon steel in the presence of acetic acid is a well-known phenomenon in the oil industry. Both chemical compounds can be produced and consumed by microorganisms during the anaerobic biodegradation of organic matter – including hydrocarbons. BIOS are composite materials made up of intact and partly degraded remains of bacterial cells mixed with poorly ordered hydrous ferric oxide minerals. BIOS are formed in response to chemical or bacterial oxidation of Fe^{+2} to Fe^{+3} which precipitates in association with bacteria cells. BIOS have reactive surfaces and act as sorbents of dissolved metal ions. Strong enrichments of Al, Cu, Cr, Mn, Sr and Zn have been reported. The BIOS metal binding potential is a function of the type, concentration and availability of iron oxyhydroxide and bacterial cell surface functional groups and their respective acidity constants. The binding strength is a function of the type, concentration and interaction of iron oxyhydroxide and bacteria surface functional groups.

X. Zhu, J. Lubeck, and J.J. Kilbane, *Appl. Environ. Microbiol.* **69**, 5354-5363 (2003).

OXIDATION OF AS(III) IN THE PRESENCE OF FE(II) BY ON Β-MNO$_2$ UNDER ACIDIC CONDITIONS

Xu Han and Ji-Dong Gu*

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The University of Hong Kong, Hong Kong SAR, China
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Arsenite [As(III)] is a highly toxic inorganic pollutant and mobile in sediment and aquifer because of its neutral, uncharged molecular state (H_3AsO_3) below pH 9.1 in soil-water environments. Oxidation of As(III) to less toxic As(V) is always observed in aqueous environment containing Mn-oxides. Fe(II), which often co-exists with As(III) in groundwater, can also be oxidized by Mn-oxides; however, its contribution to As(III) oxidation by Mn-oxides has not been reported. The objective of the present study therefore was to investigate the effect of Fe(II) on As(III) oxidation at MnO_2-water interface under acidic conditions. Kinetic experimental results showed that oxidation of As(III) could be described by pseudo-first order kinetic model and oxidation rate of As(III)/Fe(II) decreased with the increase of pH (2.0-5.0) in mono system. Competitive oxidation between Fe(II) and As(III) occurred on MnO_2 surface in the binary system, and the inhibitory effects of Fe(II) on As(III) oxidation decreased with the increase of Fe(II)/As(III) ratios. The inhibition could be attributed to the formation of Fe(III) compounds on the surface of MnO_2 and thus preventing the MnO_2 surface accessible to As(III), and the produced Fe(III) compounds sequestered more oxidized As(V) with the increase of Fe(II)/As(III) ratios. TEM results confirmed the formation of Fe compounds around or away from MnO_2 particles in both mono and binary systems, and schwerchmannite particles were detected in the mono-oxidation of Fe(II) by MnO_2, while a new kind of particle, most possibly ferric arsenate ($FeAsO_4$) as confirmed by EDX was detected in Fe(II)-As(III) binary system. On the basis of the above results, mechanism involved in the process was proposed that competitive oxidation occurred between Fe(II) and As(III) on MnO_2 first and followed by the formation of Fe compounds around MnO_2, which inhibited oxidation rate of As(III) and Fe(II) in solution. Then, As(III), but not Fe(II) in the bulk solution, could slowly diffuse through the layer of the Fe(III) compounds and access the surface of MnO_2 for further oxidation, and some of the produced As(V) was released back into solution. The present study suggested that the presence of Fe(II) played an important role in the oxidation of As(III) by MnO_2 on surface of minerals under acidic conditions.

ELECTRODEPOSITION FOR NANOSTRUCTURED LAYERS

Pietro Luigi Cavallotti

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Nanostructured layers in one dimension, two dimensions or as nanodots can be obtained through electrodeposition. Electrocrystallization must be carefully controlled in order to define it at a nano level. A rational approach to the electrodeposition processes in order to control them is presented, taking into consideration and comparing the electrokinetic behaviour of the elements and the electrodeposit structure, resulting from the electron exchange reaction at the cathodic surface. Transient electrokinetic parameters were obtained with the secondary current pulse technique, where a square galvanostatic pulse of few ms duration is overimposed on the cathode while electrodeposition is running. Two parameters are measured the transient Tafel slope and the adsorption pseudo-capacitance; whilst a third parameter the diffusive time constant must be introduced if the overvoltage does not arrive to a steady state during the short pulse period. These parameters are related to the growth of different structures; this is important for most deposition processes, but in particular for nano electrodeposition. Examples of one dimensional structures are the magnetic layers of hard cobalt alloys, of importance for magnetic recording and MEMS; examples are given for these applications. Local control of growth can be obtained with cellular electrodeposition, giving metallic fibrous single crystals with deposition of non metallic stuff at the grain boundary. Possible application for dry wear resulting in a very low friction coefficient is presented. In the case of soft magnetic layers the nano electrodeposition of two dimensional single layers, for magnetic field shielding and for GMR or spin valve multilayers, is examined and possible applications for mechanical improvements suggested. Nano electrodeposition with templates of porous anodized alumina or porous silicon is examined and possible methods to obtain highly ordered arrays of nano wires and nano dots reviewed. The obtainment of nanopowders of silver and gold is also reported with possible change of the optical properties with respect to the bulk metals.

WG 1
Development, adaptation and coupling of surface science methods for an improved analysis of the chemical processes occurring at the interfaces between materials and micro-organisms.

ADSORPTION OF FIBRONECTIN ON MODEL SURFACES OF BIOMATERIALS AND EFFECT ON CELLULAR ADHESION AND PROLIFERATION

Vincent Payet[1], Tonia Dini[1], Isabelle Frateur[1], Anouk Galtayries[1], Pascale Vigneron[2], Marie-Danielle Nagel[2], Philippe Marcus[1]

[1]Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris, Paris, France, philippe-marcus@enscp.fr
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Fibronectin (Fn) is a noncollagenous adhesive protein, from the extracellular matrix, which plays a role in cellular processes such as adhesion, proliferation and differentiation. The kinetics of adsorption of fibronectin, the quantity of adsorbed protein and the chemical modifications of model surfaces of biomaterials (Cr and Ti) have been studied. Pure Cr was studied as a model for stainless steel and pure Ti as a model for Ti alloys Quartz Crystal Microbalance (QCM) was used to investigate the adsorption of Fn under flow, at 37°C and pH 7.4 (PBS solution) with a protein concentration in solution of ~ 15 $mg.L^{-1}$. The measured initial Fn adsorption rate was ~ 0.03 $mg.m^{-2}.s^{-1}$ and an adsorption plateau was reached in ~ 40 min. Amounts of adsorbed protein were ~ 9-11 $mg.m^{-2}$ on Cr and ~ 10-15 $mg.m^{-2}$ on Ti, thus similar on both materials. Fn adsorption on both materials was partly reversible: ~ 15 % of the initially bound Fn desorbed during PBS rinsing. Surface analysis by X-ray Photoelectron Spectroscopy (XPS) showed that the protein was present on Cr and Ti oxidised surfaces and that it did not modify the chemical composition and the thickness of the passive layer. The Fn equivalent thickness was ~ 3 nm for both materials. Assuming a protein island model, the combination of QCM and XPS data showed a partial surface coverage by the adsorbed Fn (~ 0.6) with an height of the protein islands of ~ 16 nm for both materials. Static Fn adsorption was also performed, during 1h, on Cr, Fe-17Cr, and Ti as a function of Fn solution concentration (from 0 to 200 $mg.L^{-1}$). The Fn equivalent thickness after PBS rinsing was estimated using XPS data. A surface saturation was reached on all materials, for protein concentrations in solution larger than 50 $mg.L^{-1}$. The Fn layer equivalent thicknesses corresponding to the plateau were ~ 4, 6 and 5 nm for Cr, Fe-17Cr and Ti, respectively. The effect of pre-adsorbed Fn (50 $mg.L^{-1}$ in solution) on the behaviour of mouse pre-osteoblasts (MC3T3-E1), cultured in a medium with 10 % of fetal calf serum, was also studied. Cells were seeded on Cr, Fe-17Cr, Ti and polystyrene (TCPS) as a control material. MTT assays were performed to evaluate the cells viability and proliferation at 24 h and 48 h, using 2 h as a reference time. Specific DNA stainings were used to qualitatively complete these evaluations. LDH assays were carried out to estimate the cells death. These first series of tests showed that pre-adsorbed Fn improved the cells adhesion on Ti and their proliferation on Fe-17Cr.

ELECTROACOUSTIC MINIATURIZED DNA-BIOSENSOR

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A micrometer-sized electroacoustic DNA-biosensor was developed. The device included a thin semi-crystalline polyethylene terephtalate (PET) dielectric layer with two Ag microband electrodes on one side and a DNA thiol-labeled monolayer adsorbed on a gold surface on the other. A resonance wave was observed at 29 MHz with a network analyzer, upon AC voltage application between the two Ag electrodes, corresponding to electromechanical coupling induced by molecular dipoles of the PET polymer chain in the dielectric layer. It was found that the device size and geometry were well adapted to detect DNA hybridization, by measuring the capacity of the resonance response evolution: hybridization induced polarization of the dielectric material that affected the electromechanical coupling established in the dielectric layer. The 0.2 mm^2 sensor sensitive area allows detection in small volumes and still has higher detection levels for bioanalytical applications, the non-contact configuration adopted avoids electric faradaic reactions that may damage biosensor sensitive layers, and finally, PET is a costless raw material, easy to process and well adapted for large scale production. The well-balanced technological and economic advantages of this kind of device make it a good candidate for biochip integration.

PROBING POLYELECTROLYTE ADHESION BY AFM

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Extracellular polysaccharides play an important role in the attachment of bacteria and their interaction with surfaces is essential for the formation of biofilms. Here, we study by atomic force microscopy (AFM) the interaction between polysaccharides and different substrates with well-defined surface chemistry. These measurements are either performed by the so-called colloidal probe technique where a colloidal particle is attached to the end of an AFM-cantilever or by single molecule force spectroscopy where the extension and detachment from a solid substrate are measured for a single polymer chain.

For the colloidal probe technique we covalently immobilize chitosan onto the surface of a silicon wafer by means of silanes. The force profiles upon retraction are measured by colloidal probes of different surface chemistry, such as sulfate latex or silica particles. The retraction force profiles are characterized by two components, first an unspecific peak directly upon separation of the colloidal probe and second, at larger separation distances, the stretching and consecutive detachment of numerous polysaccharide chain segments bridged between the tip and the sample. This bridging adhesion can be examined on the level of the single molecule contributions, such as the number of attached chains or the distribution of the detachment forces.

In order to understand better the contributions on the level of single polymer chains, we immobilized for another set of experiments the chitosan to an AFM-tip and measured the interaction of the protruding polymer segments with various flat surfaces. We will present some first preliminary results in which desorption of chitosan from a substrate has been analyzed on the level of single monomers.

PROTEINS AND CELLS AT INTERFACES INVESTIGATED BY QCM-D AND AFM

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On one hand, the self-assembly of bacterial surface protein layers, as well as the adsorption kinetics of albumin or integrins on different substrates are relevant for bioengineering smart functional surfaces, and also get insight about fundamental molecular interactions. On the other hand, cell adhesion and cell mechanics are important for cell proliferation and cell differentiation.

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) will show us how fast proteins and cells adsorb on surfaces as well their viscoelastic behaviour; while Atomic Force Microscopy (AFM) will provide (nano)structural features of the adsorbed proteins and cells. Furthermore, we will show how the AFM can be used to study the mechanical properties of proteins and cells.

Aim of the Project is Investigation of S-protein (SbpA CCM 2177) recrystallization through surface modification and Study the kinetics of SbpA to understand the mechanism of 2D crystal formation.

Substrate induces preferential protein adsorption. Protein-sample interaction can be changed in a controlled with OH and CH3 disulfides, the difference in chain length leads to:
i) to a phase transition from a protein bilayer to a protein monolayer,
ii) induces preferential side adsorption of a protein,
iii) Changes in the crystal lattice parameters and size domain.

COMBINED AFM AND EFM FOR VISUALIZATION OF SULPHATE REDUCING BACTERIA ON THERMOSETTING RESIN / Zn COMPOSITE COATINGS

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Bacterial adhesion to surfaces is the first step in the formation of a biofilm and has been studied extensively over the past decades in many diverse applications, such as on biomaterials implanted in the human body, on ship hulls, or in food industry. Biofilms consist of microbial cells, their extracellular polymeric substances (EPS) and adsorbed organics. In addition, inorganic precipitates may originate from the bulk aqueous phase or be present as corrosion products. Physiologically diverse micro-organisms and their metabolic products, e.g. enzymes, exopolysaccharides, organic and inorganic acids, and volatile compounds, such as ammonia or hydrogen sulfide, can alter electrochemical processes at the biofilm–metal interface through co-operative effects. Sulfate-reducing bacteria (SRB) are the main group of taxonomically diverse micro-organisms which are classified as strictly anaerobic and which are distributed within two domains: Archaea and Bacteria. SRB perform dissimilatory reduction of sulfur compounds such as sulfate, sulfite, thiosulfate and sulfur itself to sulfide. Some species from the Desulfovibrio genus can grow with nitrate or fumarate as alternative electron acceptors. Compounds frequently used as a carbon source and electron donors and oxidized to acetate and CO_2 are lactate, pyruvate, malate, high molecular weight fatty acids or simple aromatic compounds, such as benzene or phenol. SRB can also degrade saturated hydrocarbons.

The work was focussed on performing AFM coupled with EFM studies in order to observe the influence of materials structure (phenol – formaldehyde resin/Zn and epoxy resin /Zn composite coatings prepared by electrolytic co-deposition) on bacteria cells (Sulphate Reducing Bacteria) attachment. Sessile bacteria on coupons were stained with 4, 6-diamidino-2- phenylindol (DAPI) and visualized by EFM as well as AFM. The best imaging conditions for AFM were assessed. Scans of bacteria attached to surfaces were performed in contact mode in air.

From the epifluorescence microscopy and atomic force microscopy images it was observe that attachment of SRB bacteria on composite coatings is lesser than pure zinc. Imagines obtained indicate an adherence process of the microorganisms on the surfaces studied with modification of the structure of the surfaces. After the attachments of the SRB on the testing surfaces the roughness decreases.

It shows that the new system for combined imaging with AFM and EFM on zinc and thermosetting resin/Zn is feasible for the application to Sulphate Reducing Bacteria on their surfaces. In addition, combined AFM and EFM can now be applied to the investigation of composite coatings.

Acknowledgments: The authors gratefully acknowledge the European Project COST Action D33 Project: Electrochemicaland biotribocorrosion studies of interfaces between materials (composites, metallic, polymeric, ceramic) and microorganisms, STSM – Grant Ref No D33 – 03620.

NANOPATTERNED XIL SUBSTRATES FOR NANO-BIO-APPLICATIONS

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The potential of surface analytical techniques in the investigation of nano-structured and nano-bio structured materials are shown. The 46.9 nm Laser at L'Aquila University is a performing technique. The deposition of 6,13 Pentacenequinone (C22H12O2) on the laser patened surfaces was studied by AFM and Photoluminescence images. A preliminary study by Atomic Force Microscopy of cytogenetic stability in a MDV-integrated chicken lymphoblastoid cell line has been presented. MDV initially infects chickens via the respiratory tract and then causes early cytolytic infection in B cell followed by latent infection in T cell. In some infections, MDV ultimately transforms CD4+ T cells and results in the formation of lymphomas in a variety of tissues. Many tumor-cell lines, including lines estabilished from leukemias, limphomas, and carcinomas, exhibit consistent chromosomal aberrations.

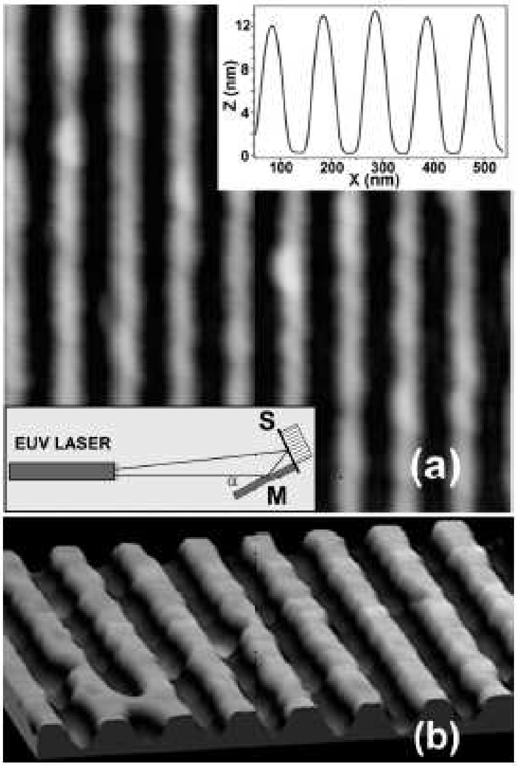

Fig. 1: AFM (plan view in (a) and three dimensional plot in (b)) images of patterned PMMA/Si(100) with 50 nm half-pitch. Lower left inset in (a): scheme of the Lloyd interferometer ((S) sample, (M) mirror). Upper inset in (a): average of 256 horizontal height line profiles taken on the corresponding AFM images. The vertical Z scale in (b) is reversed.

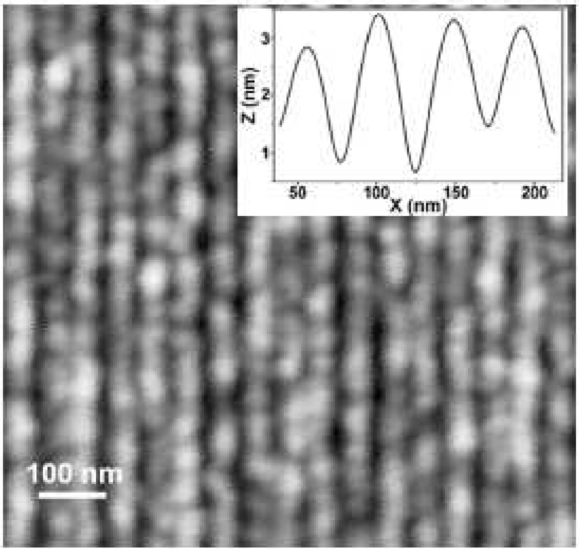

Fig. 2: AFM scan of XIL patterned PMMA/Si(100) with 22.5 nm half-pitch. Upper inset: Average of 256 horizontal height line profiles taken on the AFM image.

MATERIALS CHARACTERISTICS INFLUENCING BIOFILM FORMATION AND GROWTH

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Bacteria adhesion is a very complicated process affected by many factors: bacterial/material properties and environment. Regarding the environment it was observed that bacterial concentration versus time of exposure increases with increasing bacterial concentration and time up to a saturation level, specific for each type of surface-bacterial strain. Concentration of electrolytes, CO_2, pH and ionic strength depending on bacteria and material surface characteristics presence of Antibiotics decreases, depending on bacterial susceptibility and antibiotics concentrations. Type of bacteria cells is also important in biofilm formation and growth. Hydrophobic bacteria prefer hydrophobic material surfaces. Materials Characteristics and Chemistry of surfaces are the most important factors in bacterial adhesion and biofilm growth. The work highlights the importance of nanostructuration of surfaces and electrochemical treatments to avoid the bacteria attachment and biofim formation. Representation of cyclic steps involved in the formation of an active biofilm is time dependents and could be considered to be five. All these factors may influence bacterial adhesion by either changing physical interactions in phase one of adhesion or by changing surface characteristics of bacteria or materials.

Pure nickel and SiC/Ni nano and micro composite coatings were electrochemically deposited from a Watts bath. Electrolyte dispersions were prepared by adding SiC particles:

-20 nm for nanocomposite coatings) and
-20µm for micro composite coatings).

Sulphate Reducing Bacteria from University of Duisburg Essen Biofilm Centre, Aquatic Biotechnology were used for bacterial adhesion tests.

-Combined AFM and EFM methods can now be applied to the investigation attachment of microorganisms (Sulphate Reducing Bacteria) on nickel and SiC/Ni nano and micro composite coating surfaces.

Surface modification by nano and micro composite coatings enables the evaluation of the effect of deposition parameters and dispersed phases dimensions on bacterial adhesion.

Surface modification as nano and micro composite coatings seems to have enhanced antibacterial properties as less bacteria adhesion on nanocomposite coatings.

SRB reduce the roughness after they attaché on surfaces.

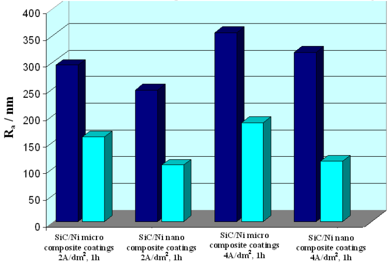

Fig. 1.
Variation of roughness before and after attached the SRB on nano and micro SiC/Ni composite coating surfaces

A rigorous study of the effects of surface chemistry / topography /morphology - structure on bacterial adhesion and protein adsorption requires a model system. We expect more interesting conclusion from future work.

WG2
Analysis of chemical and biological processes causing adhesion of macromolecules, (microbial) cells, consortia etc. to materials surfaces

ELECTROCHEMICAL AND OPTICAL METHODS IN GLUCOSE OXIDASE DISTRIBUTION AND ACTIVITY RESEARCH

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Microbially produced extracellular polymeric substances (EPS), which comprise different macromolecules, mediate initial cell adhesion to the material surface and constitute a biofilm matrix. Bacteria produce a wide range of enzymes, which are able to react with substrates beyond the cell wall. Several hypotheses were suggested, but none of them was able to explain the detailed action of microorganisms on the behaviour of metallic materials in natural seawater because it constitutes an environment in which numerous parameters can act. One of the possible mechanisms may be associated with enzymes produced by microorganisms – "enzymatic mechanism". In contrast with microbial influenced corrosion (MIC), the direct influence of enzymes is poorly documented [1,2]. It was shown that oxidase-type enzymes are involved in the ennoblement of stainless steel [3,4]. Also enzymatic systems may constitute convenient models to mimic microbial influenced corrosion, to design a new corrosion testing methods and to evaluate the behavior of metallic materials in natural waters.

In our study we propose an optical method for the evaluation of distribution and activity of Glucose oxidase (GOx) from *Aspergillus niger* (1.1.3.4) adsorbed on the different surfaces. Several GOx immobilization technologies - adhesion (i) on electrochemically cleaned gold; (ii) on gold additionally roughened with gold nanoparticles; (iii) on gold modified with self-assembled monolayer and (iv) covalent immobilization on formed self-assembled monolayer were used and compared during experimental work. The enzymatic synthesis of polypyrrole [5,6,7] and polyaniline [8] was successfully applied for visualization of active enzyme using optical methods. Electrochemical measurements also were very informative for the evaluation of GOx activity [9]. We showed that GOx adhesion on different surfaces is very important issue, and it can sophisticate evaluation of analytical signal. Distribution and activity of GOx and some other red-ox enzymes (peroxidase, lacase) on different surfaces can be visualized by synthesis of conducting polymers including polypyrrole (**Erreur ! Signet non défini.**,**Erreur ! Signet non défini.**,**Erreur ! Signet non défini.**) and polyaniline (**Erreur ! Signet non défini.**).

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NEW INNOVATIVE COMPOSITE MATERIALS OBTAINED BY ELECTRODEPOSITION WITH HIGH BIOCOMPATIBILITY

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In the last decade, porous anodic aluminium oxide (AAO) templates have been widely investigated for the manufacture of nanostructured materials, and the main reason is the possibility of controlling the pore diameter of AAO in the sub-micrometer range by simple anodization techniques, as well as the possibility of obtaining regular arrangements of the pores. Such a peculiarity, combined with their chemical nature, makes the AAO templates extremely interesting materials suitable for a wide range of applications. Porous alumina templates can be used to produce ordered arrays of metallic, semiconductor or inorganic nanodots and nanowires. Another application can be in bio- medical field.Depending on the electrolyte composition and the operating parameters (cell voltage, temperature, current density), several oxide morphologies can be obtained. Fundamental is the relationship between anodic voltage and pore size (diameter and interpore distance). Recently, it was demonstrated that the self-ordering of porous AAO film is affected not only by anodic voltage but also by the anodic current density [1]. In particular, it was showed that high electric field strength induces self-ordering since the very beginning of the anodization process. Singh et al. [2] explained the selection of the pore diameter and the interpore distance in term of the dependence of the activation energies of the interfacial reactions on the Laplace pressure at the curved interfaces due to surface energy. An additional factor may be the elastic stress caused by the volume expansion in the course of the $Al \rightarrow Al_2O_3$ reaction.

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XPS ANALYSIS OF STAINLESS STEEL AND ADLAYERS: TOWARD CHEMICAL FUNCTIONS AND MOLECULAR COMPOUNDS

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This work was performed in the frame of studies concerning the early stages of biofilm formation and the role of enzyme in biocorrosion. The results presented are focused on tentative grafting of glucose oxidase on stainless steel (316L SS). Samples were analyzed by XPS at the following stages : native stainless steel (Nat: polished, rinsed by sonication in water:ethanol mixture, dried by a nitrogen flow); same after silanization (Sil) with (3-aminopropyl)triethoxysilane (APTES), which is expected to graft NH_2-terminated silanes; Nat and Sil after contact with a glucose oxidase (Gox) solution, with or without previous treatment with bis(sulfosuccinimidyl) suberate (BS) which is expected to act as a covalent linker between the silane and the enzyme; Nat and Sil treated with BS.

The C_{1s} peak was decomposed with the background of previous works performed on systems of biological origin[1], with the constraint that all components have the same width. The components and assignments are as follows : 284.8 eV, bound only to carbon and hydrogen [C-(C,H)]; 286.3 eV, making a single bond with oxygen or nitrogen [C-(O,N)]; 287.8 eV, in amide [N-C=O] and acetal [O-C-O]; 288.7 eV, in ester [O-C=O]. The reliability of the markers of amide and proteins is supported by clear regression lines between $C_{287.8}$ and N concentrations, with small uncertainties concerning the interference of polysaccharides and nitrogen of silane.

For the O_{1s} peak, a component at 529.7 eV may be attributed to oxygen of metal oxides. The other contributions in O_{1s} cannot be safely separated in a reasonable number of components. However the respective contributions of metal hydroxide and organic oxygen (O_{org}) can be evaluated by considering that $O_{org} = C_{286.3} + C_{287.8} + C_{288.7} - N$. The composition of the oxidized stainless layer is close to (Fe, Cr)OOH.

The thickness of the organic layer can be evaluated from the ratio of the elemental concentrations of organic over inorganic constituents, measured at two different angles of photoelectron collection (0 and 60°). Moreover it turns out that (i) enzyme physical adsorption is strongly enhanced by silanization alone (Nat+Gox compared to Sil+Gox), which may due to electrostatic attraction with the protonated amine of silane; (ii) the use of a covalent coupling agent does not increase the amount of immobilized enzyme (+Gox compared to +BS+Gox); (iii) in all cases, a large amount of organic contaminants with a major hydrocarbon character is present at the surface; (iv) measurements at two photoelectron collection angles show that the enzyme retained is embedded in an organic phase in which silane is present but contaminants are dominating.

A similar approach has been used to investigate the influence of sterilization and contact with culture media on the nature of the adlayer present on stainless steel. Sharp information can be acquired on the chemical composition with nanoscale depth resolution, provided sets of data are analyzed with sound guidelines and critical spirit.

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APPLICATION OF EXTRACELLULAR POLYMERIC SUBSTANCES FOR PREVENTING MICROBIALLY INFLUENCED CORROSION

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Microbially influenced corrosion (MIC) of ferrous metals is a serious economical cost factor. It is assumed that up to 20% of all corrosion cases are caused or influenced by microorganisms, generating total costs of several billions of Euros per year [1,2]. Biofilms of sulfate-reducing bacteria (SRB) such as *Desulfovibrio* spp. can be considered as one of the main causes for MIC in anaerobic or microaerophilic environments [3].

Current conventional measures against MIC, such as periodic cleaning, biocides or cathodic protection – are expensive, ineffective or environmentally harmful. Hence, there is a demand for new, environmentally friendly concepts.

The corrosion-mitigating effect of biofilms has been described recently in literature. Their inhibiting effect is generally thought to be caused by oxygen depletion, formation of passivating layers or the adhesion prevention of detrimental microorganisms [4,5,6].

Since some of the protective effects are ascribed directly or indirectly to the EPS, an application of these compounds represents a promising new approach. Still, extensive research is required before microbial EPS can be used for corrosion inhibition over prolonged time-periods and/or in large scale.

Several bacterial EPS of different origin, extracted from SRB, *Lactobacilli* and *Pseudomonae*, as well as commercially available EPS such as Dextran and Xanthan are used to evaluate their protective capabilities against MIC on different materials. The materials tested are alloyed (X5CrNi18-10) and non-alloyed steel (C20) as well as pure iron. Their effect on MIC and the coating properties are assessed using a novel combination of atomic force and epifluorescence microscopy (AFM&EFM) with Kelvin probe microscopy, fluorescence-*in-situ*-hybridization (FISH) and weight-loss determinations. To elucidate the protective mechanisms, comparative analyses of the chemical composition of the EPS are performed.

After coating, AFM images show the formation of dense layers of EPS completely covering the surface structures of metal coupons with an approximate thickness of up to 1 µm. In MIC-simulations with *D. vulgaris* in Postgate C medium coatings with EPS extracted from cultures of this organism cause an influence on the SRB biofilm formation, probably inhibiting the microbial adhesion partially. Additionally, weight-loss determinations show a significant reduction in mass loss of up to 74%, depending on the EPS-coating employed.

However, the stability of the EPS-coatings in aqueous media has to be improved. Currently different methods for long-term fixation of the coatings are tested and evaluated using the AFM.

Acknowledgements: The project is funded by AiF Otto von Guericke e.V. (project no. AiF ZN 263 ZUTECH).

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ELECTROCHEMICAL AND AFM STUDY OF THE CELLS EFFECT ON STAINLESS STEEL AND NI-COMPOSITE COATINGS

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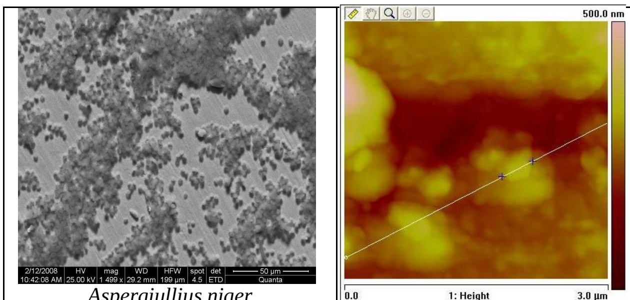
Microscopic fungi are human pathogens and serious contaminants in industry and food – processing environments. The aim of this research was to investigate how the disinfectants used for distroit the fungal cells attached of the equipment surfaces, can affect this, during the disinfection and when the time action disinfectant it is over, using Electrochemical and AFM study. It was researched the presence of fungi by artificially contaminate on stainless steel surfaces (and Ni-composite coatings) of different finishing with three major morphological fungal types: *Aspergillus niger*, *Saccharomyces cerevisiae* and *Candida* isolated from spoiled wine. Mentioned fungi were applied as models to explore aspects of the morphology of the stainless steel surface for the eukaryotic cells attachment by SEM and AFM (Fig.1). The images confirm that fungi are attached on the stainless steel surface in different way. It was found that the attached of the cells was a process with an increase in the heterogeneity and the thickness on the surface of stainless steel and Ni- composite coatings. The behaviour of cells on the electrochemical characterization of the disinfectants solution (pH 2.9 - 9.2) was investigated by Cyclic Voltammetry method. The experiments have shown the effect of different cells on stainless steel. The presence of *Aspergillus niger* cells increase the electrochemical activity of some disinfectants compared with another cells (Fig. 2).



Aspergiullius niger

Candida fungi

Fig.1. SEM and AFM images of the attached cells on stainless steel

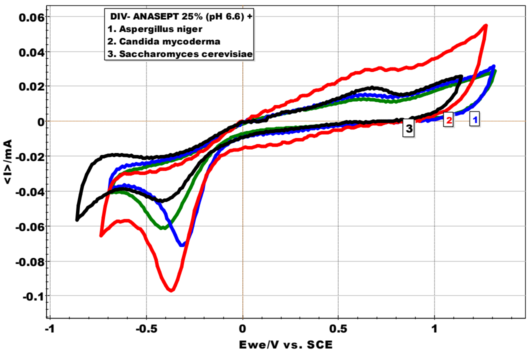


Fig.2. Cyclic voltamogram of behaviour of cells into disinfectant medium

Acknowledgment: G. Cârâc, *COST D33- STSM-D33-2446 (2008).*

HOW CAN NANOLAYERS CONTROL THE MICROBIAL ADHESION AND CORROSION?

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On iron and copper surfaces Langmuir-Blodgett (LB) and self assembled nanolayers (SAM) of amino, phosphonic and hydroxamic acids were studied in the presence of different, corrosion relevant microorganisms. The quality of self assembled and mono- and multimolecular LB layers and the inhibition efficiency of nanocoatings on microbial adhesion and biofilm formation were analyzed by different techniques. There were differences in the blocking activity of the amphiphiles applied either in LB or in SAM films. The hydrophobicity, the composition of amphiphilic molecules and the layer thickness have influenced the film's repellent activity. Correlation was found between the surface wettability and the number of adhered microorganisms: decrease in surface energy results in decrease of microbes attached to the nanolayer-modified solids.

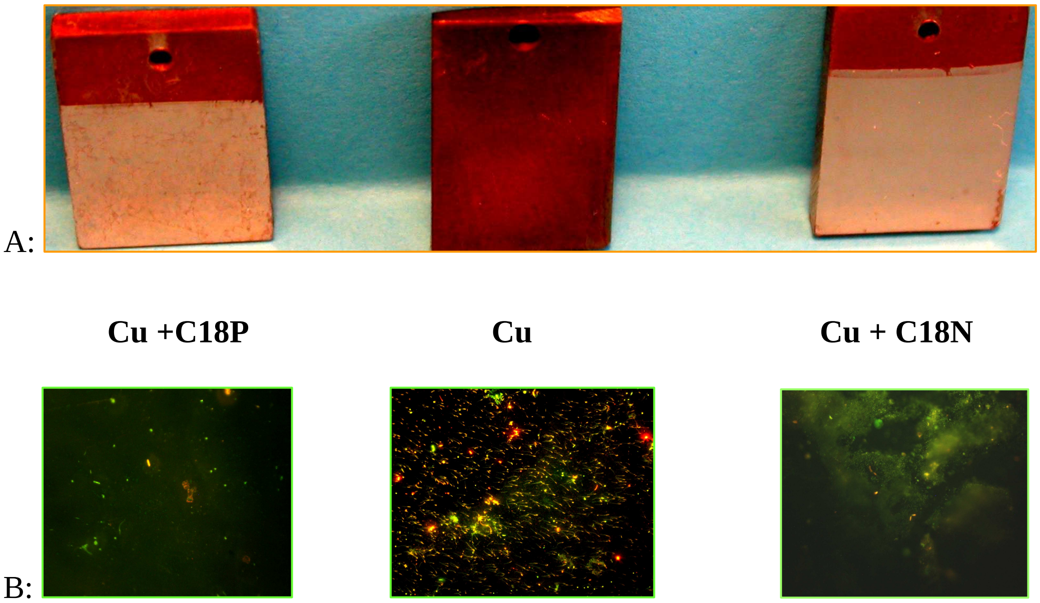

Figure 1.
A: Photos of copper surfaces with and without LB nanolayers kept in cooling water for five days;
B: fluorescence microscopic visualization of copper surfaces after 5-day-long immersion in cooling water.

APPLICATION OF SOME ISSUES RELATED TO BIOCORROSION IN BIOFUEL CELLS

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In some particular cases bio-corrosion of metal surfaces is related to catalyci action of red-ox enzymes present in microorganisms. This issue can be successfully exploited in development of alternative power sources – biofuel cells. Some enzymes are able to transfer electrons directly to conducting surfaces, this so called "direct electron transfer" (DET) is a unique feature which is exhibited not by all red-ox [1]. The possibility of DET between enzyme and the electrode surface could pave the way for superior reagentless, noncompartmentised, mediator-free biofuel cells, as it obviates the need for mediators and allows an efficient transduction of the electrical current [2]. DET is highly beneficial in the development of enzymatic and microbial biofuel cells [3]. In the review article, hemoproteins, which are able to directly transfer electrons to the surfaces of conducting supports, are briefly overviewed and characterized [4]. The main focus is paid to the application of heme-c containing enzymes in biofuel cell design. Some historical steps and recent developments in biofuel cell design are presented. Various designs of biofuel cells are overviewed. Some possible applications of biofuel cells are presented and/or predicted and discussed. Problems and challenges in biofuel cell design/application are identified and some possible directions to solve recent problems in biofuel cell development are discussed. The application of enzymatic biofuel cells as model systems/tools for advanced study of enzyme-based bio-corrosion is predicted.

Acknowledgement
Support by COST action D33 is acknowledged.

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COMPARISON OF THE ELECTROCHEMICAL BEHAVIOR OF STAINLESS STEELS IN ABIOTIC AND BIOTIC SEAWATER

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Since LaQue has pointed out that seawater, directly provided from ocean, is more aggressive than seawater carried to laboratory and than the artificial one, the influence of bacteria on corrosion phenomena and of corrosion phenomena on microbiology were recognized. Engineers, chemists, physics, biologists and traders are now collaborating in lots of works to try to understand, to monitor and to control interactions between corrosion and microbiology.

Corrosion potential of passive materials exposed to water environment and in absence of localized corrosion is characterized by values distributed in wide ranges. Moreover, ennoblement of the corrosion potential vs. exposure time has been observed in different environment, e.g. natural and artificial seawater or hydrochloric acid solution.

In this work, the evolution in time of the anodic behavior of passive materials and particularly its effect on the corrosion potential in natural waters are investigated. Different hydrodynamic and biological conditions are considered. The distinction between the kinetics of the cathodic and anodic process and experimental polarization curves is highlighted. A careful analyses on the equilibrium between cathodic and anodic current in the experimental polarization curve is carried out to relate the ennoblement of the corrosion potential to the aging of the passive film. A weak inhibition of the anodic process rather than an enhancement of the cathodic one can justify the evolution of the corrosion potential.

WG3
Understanding of the elementary steps leading to biocorrosion, biofouling, biofilms, bioleaching etc. in order to inhibit or improve the respective processes: Applications in practice

EXOPOLYSACHARIDE EPS180
AS ANTI-CORROSIVE ADDITIVES FOR COATINGS

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The corrosion of iron and its alloys causes economical loss resulting in a yearly cost of billions of euros. The use of heavy metals and heavy metal based anti-corrosive compounds in organic coatings has been known for decades. However, environmental reasons and health concerns have restricted and even banned the use of these compounds. It was shown that some Exopolysaccharides (EPS), especially homopolysaccharides, exhibit anti-corrosive properties on steel. EPS are large sugar molecules (50 to 50,000 sugar units) produced by a variety of microorganisms. Homopolysaccharides produced by lactic acid bacteria are synthesized by a single extra cellular sucrose enzyme using only sucrose as substrate. They can be produced out of sucrose in large quantities (bulk scale). Moreover, in the project their structure has been elucidated and modified allowing optimization of their physicochemical properties. Electrochemical measurements have been performed interactively with the modifications to obtain maximal protective properties.

From these activities an EPS, coded EPS180 has been developed has one to be used in protective coatings.

In a second part of the project Electrochemical Impedance Spectroscopy together with salt spray tests has been used to optimize and assess the performance of coatings containing the EPS186.

Coatings based on two different types of binder (both water borne) have been investigated:

- Epoxy with EPS186 replacing zinc phosphate; intended for maritime applications.
- Styrene-acrylic copolymer with additions of EPS186; intended for atmospheric applications.

From the promising results of these laboratory tests it was decided to scale up the production of EPS180 and to perform formulation and application of the EPS180 coatings in practice.

For this aim the “bioprimer” coatings have been applied on a dry-dock in Delfzijl. The epoxy based coating was applied in the area of the dry-dock which is regularly submersed by seawater. Both types of coatings were also applied on the area above the water level. Conventional solvent and water based reference systems were added to the experiment. The area of each coating sample was 1 m^2.

After two years of exposure, in these extremely aggressive circumstances, the results were quite promising: the protective performance of the experimental coatings was at least as good as that of the reference systems. Exposure of the same systems on panels in Den Helder, near the seawater confirms these results.

AN ACCOUNT OF THE ANTIMICROBIAL ACTIVITY OF AN A HELICAL PEPTIDE AND AN EVALUATION OF ITS USE AS A SURFACE COATING ON FABRIC AGAINST BACTERIAL CONTAMINATION

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Antimicrobial peptides form an ancient host defence mechanism which is utilized by a wide range of living organisms. It is well established that α-helical antimicrobial peptides (α-AMP's) are produced by a diverse range of organisms and form a crucial component of their innate immune system by killing a wide range of microbes ranging from bacteria to parasites. The vast majority of these peptides are cationic, which facilitates their targeting of the anionic microbial membrane. They are also amphiphilic, which promotes their partitioning into these membranes, thereby compromising membrane integrity and inducing cell death. This COST motivated project looks at the antimicrobial activity of an α helical peptide and investigates its potential application as an antimicrobial coating on fabric. An account is presented of the origin, nature, properties and mode of action of an antimicrobial peptide, aurein 2.5. Experimental protocols for the estimation MIC of values against selected Gram positive and Gram negative bacteria in their planktonic and sessile phases are described. A washed cell contact technique was used for the MIC evaluations and a method for generating early monoculture biofilms in a tissue culture chamber is presented. The implications of the results of this work are discussed. An account of work using a Langmuir-Blodgett trough is presented to provide data relating to changes in interfacial surface pressure with varying concentrations of the peptide. Interactions of aurein with monolayer 'membranes' i.e. those whose phospholipid components mimic those of selected bacteria are described and results presented. Membrane perturbation mechanisms of the aureins are reviewed

The results obtained from the assessment of the antimicrobial activity of aurein 2.5, led to its being considered as an antimicrobial coating for use on fabric. To this end, an account is presented of its potential use for this purpose, using a modified version of AATCC Test Method 100-1998 (Antibacterial Finishes on Textile materials). The modified method is described and the results are evaluated.

The results of this investigation show MIC values of 30µM against planktonic cells and 125µM against early biofilms. As a result of the Langmuir-Blodgett trough work, evidence is provided of monolayer interactions of aurein 2.5 and strong interaction with lipid extracts of target microorganisms. The results of the AATCC Test method experiments show that when the aurein was applied to the surface of a cotton fabric and allowed to dry, this treatment reduced a challenge population of test organisms to zero when compared to untreated controls. Furthermore evidence is reported of a 90% reduction in a challenge population when treated fabric was stored for periods of three weeks and three months at room temperature prior to testing.

BIOREMEDIATION OF RADIOACTIVE WATER IN NUCLEAR POWER PLANTS: PRESENTATION OF FINAL RESULTS

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Previous research carried out at the Cofrentes Nuclear Power Plant (NPP) showed that in the water of the Spent Nuclear Fuel (SNF) pools there are microorganisms which colonize metallic materials immersed in the pools and form biofilms. We observed that these biofilms retain radionuclides, so they could be used to decontaminate radioactive water in a bioremediation process. In order to analyze the effectiveness and the economic viability of this process two bioreactors were designed and installed on-line in the water cooling system of the SNF pools in the fuel building at the Cofrentes NPP. Inside each bioreactor 12 stainless steel balls were located, and were removed periodically for analysis along 22 months.

Scanning electron microscopy (SEM) revealed that the stainless steel balls were progressively colonized by filamentous and long rod-shaped bacteria that formed biofilms on their surface. After 15 months corrosion products were observed on the materials; at the end of the study the material was corroded and no microorganisms could be seen on the stainless steel surface.

The radioactivity of the biofilms was determined by gamma-spectrometry. We found that the biofilms started to retain radionuclides after 3 months and accumulated them until about 300 days when radioactivity began to decrease. The main radionuclide detected in the biofilms was ^{60}Co. After 22 months radioactivity came back to almost the initial levels, probably due to biofilms detachment as the SEM images demonstrated.

The identification of bacteria through molecular techniques such as cloning and sequencing of a discrete fragment of 16S rDNA gene showed that biofilms were formed by a low diversity of nonculturable microorganisms. A total of 502 clones were sequenced, belonging most of them to *Gammaproteobacteria*, *Alphaproteobacteria* and *Actinobacteria* classes. In our opinion metagenomic studies searching for relevant enzymatic activities implicated in the radionuclides retention would be very useful for the enhancement of those activities.

Procedures developed by this research are of interest for the decontamination of radioactive waters in the Nuclear Power Industry.

BACTERIAL INTERACTIONS WITH AG-BEARING SURFACES: AG-PD COATING AND AG-BEARING STAINLESS STEEL

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In this work, silver-palladium surfaces and silver-bearing stainless steels were designed and investigated focusing on electrochemical principles to form bacteria inhibiting effects. The biofilm inhibition efficacy and the biofilm inhibition mechanism of silver-palladium surfaces under conditions of low and high bacterial load were studying by using batch and flow-chamber setups respectively. The influence of silver additions to type 316 austenitic stainless steels has been investigated focusing on bacterial inhibition, mechanical properties, and corrosion resistance.

For silver-palladium surfaces, experiments showed that the surfaces can inhibit bacteria and biofilms due to generation of micro-electric fields and electrochemical redox processes from the surfaces. For silver-bearing stainless steels, experiments showed that silver addition to stainless steels can improve bacteria inhibiting property due to the release of toxic levels of silver from the surfaces, but mechanical and corrosion properties are slightly impaired as compared to traditional stainless steels. However, highest efficiency of these surfaces may be achieved under conditions, where appropriate cleaning practices can be applied, as bacterial microcolonies may occur, if these surfaces become covered with a conditioning layer of dead surface-associated bacteria.

Experiments also showed that surface-associated bacteria greatly increased silver dissolution from the silver-bearing surfaces due to the interactions between cell components and the surfaces, and the amount of surface-associated bacteria enhanced this effect.

STUDY OF DENTAL TISSUES/RESIN-BASED MATERIALS INTERFACE

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Dental composites based on diacrylic resins (RDC) and resin-modified glass ionomer cements (RMGICs) have different characteristics and features, which impose the use of one or other material for a specific application. *The purpose* of the present study was to elaborate a series of novel experimental RDC and RMGICs and to investigate the influence of the resins composition upon the tooth / RDC (RMGIC) restoration interface. The resin matrices of RDCs were prepared using an aromatic urethane tetramethacrylate Bis-GMA analogue, and a mixture of Bis-GMA superior oligomers respectively. Triethyleneglicol dimethacrylate (TEGDMA) was used as diluting monomer.

The photopolymerizable RMGICs were prepared in the powder-liquid system, the powders representing mixtures of superficially active glasses and the liquids representing aqueous solutions of polyalchenoic acids, 2-hydroxyethyl methacrylate (HEMA) and a modifying monomer, in different ratios. Class V cavities (3 mm diameter and 1.5 mm depth) were prepared in 20 extracted human premolars and molars. The RMGICs were applied to the cavities with or without previous use of an adhesive. The teeth were sectioned on an Isomet Low Speed Saw-Buechler LTD machine. SEM photomicrographs of the interfacial region between the tooth and RDC (RMGIC) were performed.

The composition of RDCs , and respectively RMGICs highly influenced the adhesion to the dental tissues. A better adhesion of RMGICs was obtained in the case of using the modifying monomer in the composition and in the case of prior application of the adhesive. The best adhesion of RDCs to tooth tissues was obtained in the case of using the adhesive system and the Bis-GMA urethane-tetramethacrylic monomer. This behaviour could be explained by the better compatibility between the Bis-GMA analogue in the bonding, respectively the base monomer in the composite and the primer. The present results show that Bis-GMA analogue can be successfully used in formulations for restorative dentistry.

BIOFILMS IN MICROTITER PLATES: WHAT DO WE MEASURE?

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Experimental systems to study biofilms can be costly and time consuming, and may have reproducibility problems, particularly in unexperienced hands. Microtiter plates are single-use polymeric receptacles presenting at least 96 casted wells, whose 100-400 μL capacity that can be automatically filled, incubated and *in situ* measured. Together with their more and more sophisticated readers or analyzers, microplates offer the chance to perform simple, unexpensive and high throughput assays for very diverse types of biological and chemical labwork. They are increasingly used for biofilm work, particularly to test antimicrobials.

The methodologies involved, however, can yield results that are tricky to interpret, particularly when comparing different organisms. We have focused our attention on the variations of the technique and the culture conditions, and the different rates of cells and EPS found in biofilms. S*taphylococcus aureus* and *Pseudomonas fluorescens*, both outstanding biofilm formers and highly relevant organisms for food safety and quality, respectively, have been utilized.

EPS180 PROPERTIES IN CONCRETE AS ANTI-CORROSION AND ANTI-MICROBIAL REAGENT: A CHALLENGE?

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Concretes are artificial building materials that are principally made of cement, aggregate, water and various admixtures. These materials are sensitive to many factors inducing the degradation of the cement matrix and the steel reinforcements. The weathering factors can be physical, chemical and/or biological ones. Sound concrete constitutes a protective environment for the steel reinforcing bars due to its pH about 13: the steel is passivated. However, this passive layer can be broken by a decrease of the pH or a high concentration of chloride ions that can lead to the corrosion of the steel reinforcements. EPS 180 are natural glucan exopolysaccharides produced by glucansucrase GTF180 enzyme from a gram-positive bacterium: *Lactobacillus reuteri* 180. Research projects carried out in TNO showed that the EPS 180 have anti-corrosive and anti-adhesive properties on steel.

This project aims to evaluate the influence of EPS 180 on the corrosion of the low carbon steel used as reinforcement of concrete. The samples are 8 mm diameter C15 steel bars embedded in three different cement pastes (CEMI, CEMIII and CEMV). The EPS are considered like an admixture and included in the cement batch. Four EPS contents are tested for each cement base: 0%, 0.5%, 1%, 2.5% and 5%. The reference samples are the three cement pastes without EPS. The samples are immersed in flowing natural seawater in the TNO laboratory (Den Helder). The corrosion behaviour of the samples is tested by Open Circuit Potential (OCP) measurements, Electrochemical Impedance Spectrometry (EIS) and the Polarization Curves (PC) are determined.

OCP tests show that the EPS have a positive influence on the reinforcement resistance to seawater environment after 1 week immersion for all the cement bases. The corrosion potential is always higher for the samples containing EPS than for the samples without EPS.

The polarization curves confirm that embedded C15 steel in cement matrix is passivated, but a pick on the polarization curves appears for a potential about -0,38V/Ag-AgCl electrode for all the cement bases. The presence of EPS does not induce a decrease of the corrosion current but prolongs the plateau of anodic passivation until the end of the test.

EIS tests show that the impedance of the CEMI samples with EPS is higher than the one of the reference samples. The results obtain with the CEMIII samples do not allow any conclusion about the influence of the EPS on these cement base. The CEMV show that the EPS content present an optimum: the 0.5%, 1% and 2.5% EPS samples show higher impedance than the without EPS samples for all the frequency but the 5% EPS samples show lower impedance than all the other samples.

The EPS show then anti-corrosive properties in cement at short term exposure in seawater, this study has to be continued to evaluate the influence of the EPS for long term immersion, their anti-adhesive properties and the porous network evolution of the cementations matrix due to the use of EPS.

In the frame of the D33 COST Action, a three weeks short term scientific mission was carried in the TNO laboratory in Den Helder about this project.

ELECTROCHEMICAL STUDIES OF TITANIUM IMPLANTS IN CHLORIDE SOLUTION

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Pure titanium (Ti) and titanium alloys are frequently used as dental and orthopedic implant materials due to their excellent mechanical strength, chemical stability and biocompatibility. The biocompatibility of titanium is closely related to the properties of the surface oxide layer. Anodic and thermal oxidation of Ti has been widely applied for the production of Ti/TiO_2 implant materials in order to improve the physical and chemical properties of the bulk metal. In this work cyclic voltammetry and electrochemical impedance spectroscopy have been used to investigate the corrosion behaviour of Ti/TiO_2 implants in solution simulating the physiological conditions. The minor morphological changes in the Ti/TiO_2 layer - in vitro and in vivo conditions- were investigated by SEM studies.

Cyclic voltammetric measurements indicated that TiO_2 layer is compact and due to the decreased electrochemical activity of the bulk metal, the Ti/TiO_2 samples act like inert electrodes. It was also found, that the interaction of the implants with the human body and the implantation procedure of the osteosynthesis plates caused minor local damages in the oxide layer. CV and EIS measurements have detected repassivation of these active sites.

Metallic implants in the human body act as passive surface therefore it is prone to bacterial adhesion potentially and can cause deep body infection. Lot of efforts is made to utilize the antibacterial behaviour of silver coating to prevent the implanted assisted infection and to inhibit the bacterial growth on the metallic implants. The data of current animal experiments showed that the infection rate of silver coated medical devices have been reduced. This lecture discusses the preparation of silver coatings on metallic substrates by pulse current technique and the relationship between the pulse plating variables and the morphology. Finally the antimicrobiological effect of the silver deposits will be presented.

MICROBIALLY INFLUENCED CORROSION IN SHIPTANK ENVIRONMENTS

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As intensively discussed in literature, corrosion in ship tank environments is shown to be a serious problem for decades. The study of Microbiologically Influenced Corrosion (MIC) is gaining increasing interest. However, until today no clear explanation and identification of the corrosion process influenced by micro-organisms is found. The experiments were performed in a lab scale model system for electrochemical measurements in combination with MIC causing micro-organisms. Experiments were carried out applying Electrochemical Impedance Spectroscopy (EIS) as well as Epifluorescence Microscopy (EFM) to relate electrochemical techniques with microbial growth patterns. This study compared the corrosion behavior of ASTM A131 Steel, grade EH36 exposed to seawater, artificial seawater with and without nutrients in presence and absence of a marine aerobic *Pseudomonas* bacterium and an anaerobic sulfate reducing bacterium (SRB) *Desulfovibrio indonesiensis*. The bacterial cells preferentially attached themselves to the steel surface to form patchy biofilms, as observed by EFM. The interactions between bacteria and the metal surface were monitored by EIS in different solutions with and without the attachment of bacteria, which provides important information on the microbial process occurring on the metal surface, particularly the role of Extracellular Polymeric Substances (EPS) on the corrosion process. By coupling electrochemical analysis with microbiological tools, the time depending transport processes occurring within the biofilm/metal interface were characterized which in turn relates to the corrosion process on the steel surface.

COST D33 – PRO'S AND CON'S, AN IMPRESSION OF EXPERIENCES FROM INDUSTRY

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COST Action D33 has been running for about 4 years. Unfortunately participation from industry has not been abundant. A review will be given from initial incentives and objectives for participation as well as the acquired results so far.
Pro's and Con's, an impression of experiences from industry.

POSTERS

CHARACTERIZATION OF AN ANTIMICROBIAL PEPTIDE AUREIN 2.5 WITH BACTERIAL MEMBRANES

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The search for new antibiotics has recently been focused on α-helical antimicrobial peptides (AMPs) that exert their activity *via* the invasion of bacterial membranes. Aurein 2.5 (GLFDIVKKVVGAFGSL-NH_2) is an uncharacterized antimicrobial peptide isolated from *Litoria aurea* and *Litoria raniformis* which exhibits broad range antimicrobial activity. However, the ability of the peptide to interact with bacterial cell membranes has not been addressed in detail. Aurein 2.5 was strongly antibacterial, exhibiting a minimum inhibitory concentration of 30 μM against planktonic cells for both *Bacillus subtilis* and *Escherichia coli*. However, when directed against bacterial biofilms, aurein 2.5 exhibited an MIC $\geq$ 125 μM against both bacteria. The peptide's mode of membrane interaction was investigated using a Langmuir Blodgett trough. At an air / water interface, aurein 2.5 was found to be strongly surface active with maximal surface pressures of 25 mN m^{-1}, which is comparable to that of other AMPs from amphibian sources. Peptide isotherms showed that the molecular areas were consistent with the adoption of α-helical structure orientated either perpendicular (1.72 nm^2 $molecule^{-1}$) or parallel (3.6 nm^2 $molecule^{-1}$) to the interface. The peptide induced stable surface pressure changes in monolayers that were mimetic of membranes of *B. subtilis* (*circa* 9 mN m^{-1}) and *E. coli* (*circa* 5 mN m^{-1}) whilst compression isotherm analysis of these monolayers showed $\Delta G_{Mix} > 0$, indicating destabilisation by aurein 2.5. The peptide readily inserted into zwitterionic DOPE and anionic DOPG monolayers, inducing surface pressure changes *circa* 6 and 7 mN m^{-1} respectively suggesting that the membrane interactions of aurein 2.5 were driven by amphiphilicity rather than electrostatic interaction. Based on these data, it was suggested that the differing ability of aurein 2.5 to insert into membranes of *B. subtilis* and *E. coli* was probably related to membrane-based factors such as differences in lipid packing characteristics.

ZRO_2/CO NEW FUNCTIONAL BIO COMPOSITE COATINGS

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Zirconia – cobalt functionalized surfaces have potential applications in industry and bio-medical devices. The attempts to obtain new high performance materials led to the development of a class of products known as composite materials. The main objective in developing the composites is to ensure performance characteristics and properties, beyond the limits known for metallic and nonmetallic materials normally used. It is easy to describe a composite as being made from matrix material in which there are added one or more types of reinforcement staff, or simply the matrix is filled with other materials considered allowance staff. So far the main reason why composite materials have been developed with metal matrix was to increase resistance and tenacity of the components. Other important improvements to such features as buffer capacity, specific weight, wear resistance, thermal expansion coefficient, and working capacity at high temperatures may be achieved by the advantageous combination of addition /allowance materials.

The paper presents the obtaining and characterisation of composite coatings in Co matrix with zirconium oxide by electroplating process. The AFM images of a ZrO_2-Co composite layer obtained at 23 mA/cm2 current density are presented in Fig. 1., compared with pure cobalt coating in the same conditions obtained (Fig.2.).

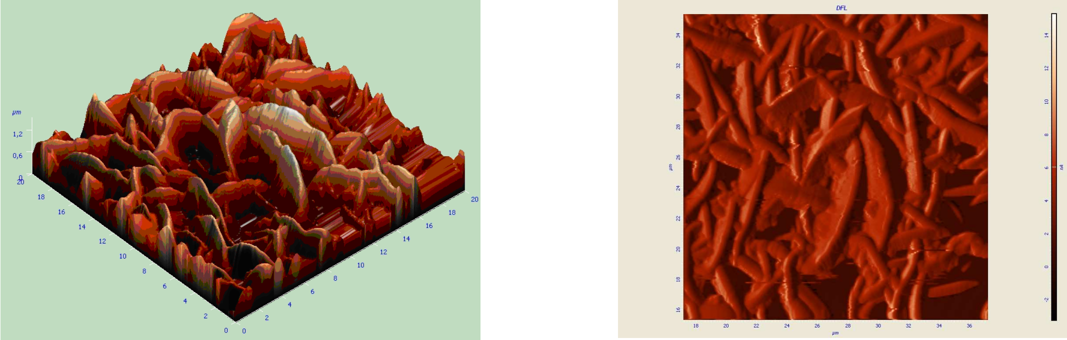

Fig. 1. ZrO_2 / Co composite layer obtained at 23 mA/cm^2 and 20g/L ZrO_2 in the electrolyte (20 µm thickness)

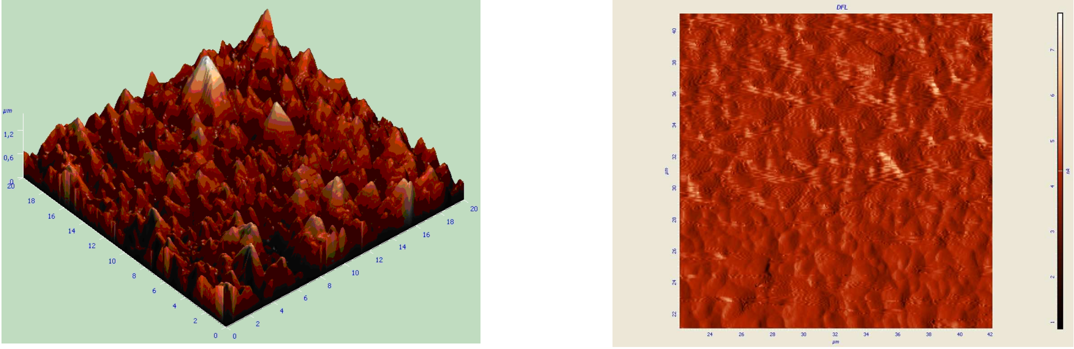

Fig. 2. Pure Co coating obtained at 23 mA/cm^2 (20 µm thickness)

The presence of ZrO_2 dispersed particles in the cobalt matrix enhances the properties of composite coatings.

CATALYTIC EFFECT OF GLUCOSE OXIDASE AND GOLD NANOPARTICLES ON BIOCORROSION PROCESSES

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Biocorrosion is an interfacial process relating with biofilm's formation and surface's degradation [1]. The addition of glucose oxidase (GOx) and glucose, of hydrogen peroxide and/or gluconic acid could strongly modified the properties of the oxide film and have the influence on the kinetics of the reductions occurring on the surface: the donor density in the artificial freshwater increase, that is to say an increase of available electrons near to the surface [1,2].

Metallic nanoparticles are often used in non-enzymatic catalysis and in biosensor design [3]. In some particular cases they could not only increase electron transfer rate between enzyme and an electrode surface, but could act like nano-scaled electrode for the assembly of biomolecules [4]. Also gold nanoparticles (Au-NPs) can be used as very efficient red-ox mediator suitable for biosensor design [5].

Various combinations of gold nanoparticles, glucose oxidase, red-ox mediator N-methylphenazonium methyl sulphate (PMS) and red-ox-dye 2,6-dichloroindophenol sodium salt hydrate were tested. It will be presented that the enzymatic reaction rate of GOx in presence of Au-NPs is by 1.48 times higher than in similar solution in absence of nanoparticles, and Au-NPs in the solution with PMS could increase the catalyzed reaction rate of protein by 1.7 times [6].

Electron transfer properties of Au-NPs with GOx have been widely used in constructing electrochemical biosensors [7], where electrodes might be successfully modified with biomolecules and nanoparticles. These combinations are of considerable interest in the fields of biotechnology, bioanalytical chemistry and in biocorrosion processes. The amperometric glucose sensor based on glucose oxidase immobilized on gold nanoparticles modified carbon rod electrode was created and tested in presence and absence of PMS in sodium acetate and sodium phosphate buffers (pH 6.0). The influence of diameter of Au-NPs on the sensitivity of biosensor, its stability and catalytic effect on biocorrosion processes was investigated and will be presented.

Acknowledgement: Support by Lithuanian State Science and Studies Foundation Post-doc program (Nr. S-6/2007) is acknowledged.

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INFLUENCE OF UHMWPE/CO COMPOSITE COATINGS ON BIOFILM FORMATION, BIOCOMPATIBILITY AND DEGRADATION

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The work aims to obtain composite coatings in cobalt matrix with dispersed phase UHMWPE (ultra high molecular weight polyethylene). All coatings were obtained on stainless steel plates. UHMWPE was selected as surface modifier element, due to its high biocompatibility and excellent wear behaviour.

The electrodeposition of these metal and composite layers is a process consisting of inclusion of UHMWPE particles in the cobalt matrix during electroplating process. The dispersed particles were suspended in the deposition bath within the metal which electro-crystallizes and forms the metal matrix. By means of the potentiostat a number of five current densities were applied during deposition as follow: 23mA/cm^2, 48mA/cm^2, 72mA/cm^2, 96mA/cm^2 and 120mA/cm^2.Obtaining these layers of pure Co and Co - UHMWPE was done in an electrolyte solution, which has the following composition: $CoSO_4 \cdot 7H_2O$ 300g / L, $CoCl_2 \cdot 6H_2O$ 50g / L, H_3BO_3 30g / L and dodicy 0,157 g / L and a pH of ≈ 5. For the electrolyte with UHMWPE two concentrations were used: 20g / L and 30 g / L.

Keeping the UHMWPE particles in Co electrolyte suspension, was provided by magnetic stirring at a rotation speed of 300 PRM. The deposition time was 30 min, and 60 min. respectively.

After processing the results, it was noticed that increasing current density and maintaining the deposition time more, from 30 minutes to 60 minutes, the thickness of the layer deposited on pure cobalt or composite based on cobalt and UHMWPE and ZrO_2 increased as well. The results were confirmed by XRF measurements and they are shown in the figures below.

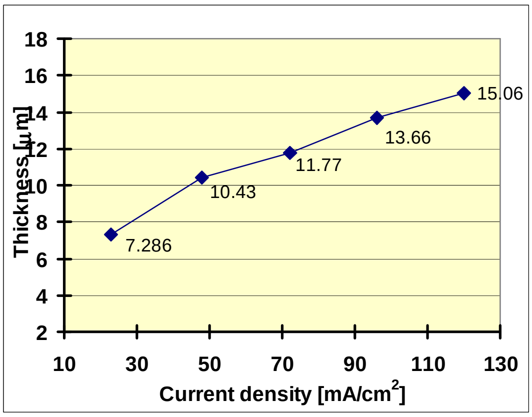

Fig. 1. Pure cobalt coating thickness versus current density

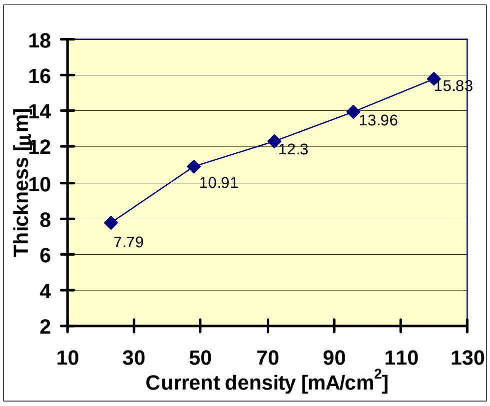

Fig. 2. Co+UHMWPE composite coating thickness versus current density

The SEM and AFM images of Co + UHMWPE coating, on stainless steel, show the presence of dispersed phase UHMWPE (polyethylene of high molecular weight) in the cobalt matrix. Also, the images AFM reveal the increase roughness at once the increase times, concentration and current density, respectively.

NANO-COMPOSITE COATINGS – FUNCTIONAL SURFACES IN DECREASING THE BACTERIAL ADHESION - SURFACE STUDY

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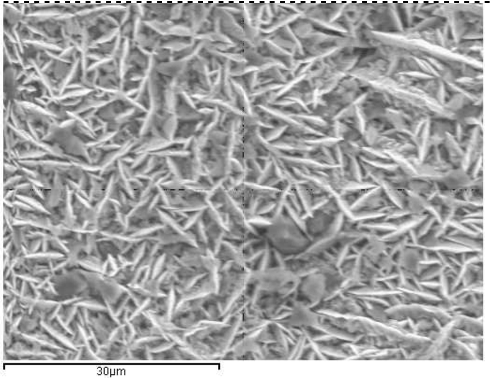
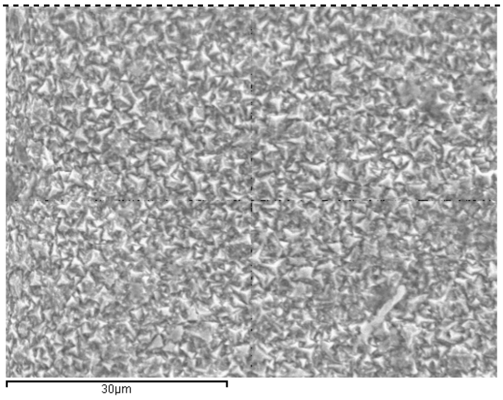
The paper presents the obtaining of composite coatings in Co matrix with zirconium oxide by electroplating process. The suspension is prepared by adding 50 g/L ZrO_2 particles in the electrolyte solution. The ferrous metal coatings (steel, cast iron) are widely used for protection against corrosion. The cobalt electrolytic deposition from the aqueous salt solutions of this metal, with its strong electronegative potential, is possible because the hydrogen features a higher overvoltage than cobalt and, under normal electrolysis conditions, is hardly present at cathode. The electrodeposition process provides a rigid control over the layer thickness and the deposition rate uniformity. The structure of the cobalt depositions depends on the pH of the electrolytic; at low pH values the deposits have cubic and hexagonal structure patterns, and at high pH the hexagonal structure prevails. The electrochemical cell for co-deposition is composed of an anode represented by the 99.9% cobalt plate, the cathode represented by a steel plate and the electrolyte solution which has the following composition: cobalt sulphate 20 g/L, cobalt chloride 300 g/L and boric acid 30g/L with a pH value equal to 4. The particles were maintained uniformly in the suspension with a magnetic stirrer at a rotation speed of 500 rpm. By adding the particles of ZrO_2 in the cobalt plating bath, the coating thickness obtained in these conditions vary from 2.75 μm to 28.72 μm at a current density from 5.7 mA/cm^2 to 45.7 mA/cm^2. The morphology of the composite surface layers is different from the pure cobalt layers; the regular crystalline structure characteristic to pure cobalt layers are disturbed by the zirconium oxide particles that grow during electrodeposition.



SEM image of ZrO_2/Co composite coatings



SEM image of pure Co coating

The correlation between electrodeposition parameters and the coatings properties (thickness, corrosion, microhardness) were made. Co-deposition of dispersed micro and nano sized particles with metals during electroplating process influences the structure and surface morphology of composite coatings obtained. As a result the corrosion and properties o such coatings are improved. As a conclusion dispersion strengthening in coatings, could be a way to improve the properties of cobalt electrodeposits, taking into account the biocompatibility of such materials (metalic matrix, as well as the dispersed phase).

STUDY OF TIO$_2$/HYDROXYAPATITE STAINLESS STEEL – NANOCOMPOSITE COATINGS AT THE CELLS ADHESION

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One of the most effective methods to improve the corrosion resistance and the biocompatibility of the metals is to deposit a protective bioactive ceramic coating layer on the metal surface [1]. In the present investigation, an attempt has been made to deposit porous TiO_2 thin films on 316L SS. The electrophoresis synthesis of TiO_2 was performed in an electrochemical cell with three electrodes [2]. The bath contains H_2SO_4 and TiO_2 particles at pH of 1.4. The deposition was performed at room temperature at (-1.43) V potential versus Ag/AgCl (RE). A simple SBF solution with high calcium and phosphate ion concentrations was used for biomimetic coating study of HAp and kept at 37°C and pH of 7.5. In order to simulate the in vivo process, the specimens coated were directly immersed into SBF solution, taken out of the solution after 3, 5, 7 and 21 days of immersion, rinsed with deionized water and dried at 60°C for 1h. The coating formed on 316L SS substrate was characterized by SEM, AFM), X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). The AFM imagesof the TiO_2 coating on 316L SS revealed the changes in surface topography of thin films due to the heat treatment at 400°C. The results reveal that the difference between both thickness values is due to the evaporation of the solvent and organic components. The surface roughness increases with increasing time deposition and due to the formation of aggregates of the particles by thermal treatment. From the XRD patterns it can identify the specific peaks of anatase phase of TiO_2 coated on 316L SS with (101), (110), (004), (200) and (211) crystallographic planes. The SEM micrograph (fig.1) indicates a good behaviour of TiO_2/316L SS system by immersing in SBF solution due to the incorporation of Ca^{2+} and PO_4^{3-} ions during 3 days. The concentrations of specific ions were measured by EDX analysis and the ratio Ca/P was calculated at 1.85 in good agreement with theoretical results.

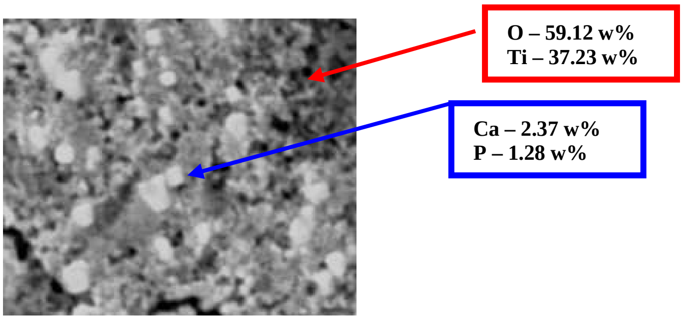

Fig.1. The surface morphology of HAp coated substrate after subjecting to immersion in SBF solution (3 days) and the characteristic elements detected by EDX analysis.

Acknowledgment: Ph.D. stud. A. Cantaragiu, *COST D33- STSM-D33-04478 (2009).*

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BEHAVIOR OF CELLS ADHESION ON THE STAINLESS STEEL 304 INTO DISINFECTANT MEDIUM

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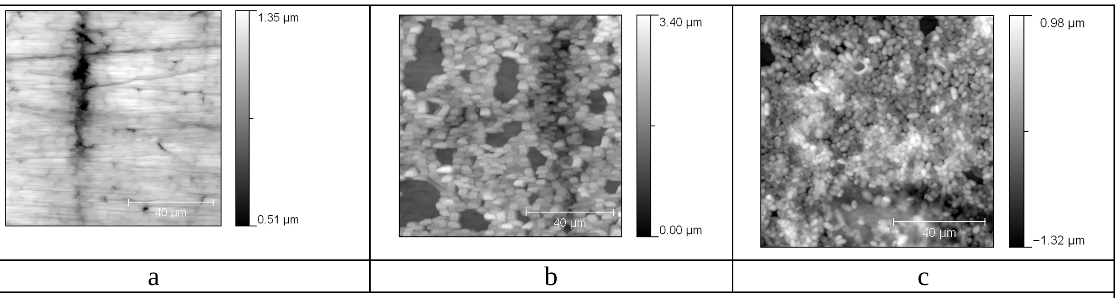
In many food industries, production lines are daily cleaned [1] and disinfected [2]. Many factors affect disinfection efficacy in food line products, e.g. pH, concentration of the disinfectant, contact time etc. Alloys 304 and 304L Stainless Steel are the most familiar and the extensive used in food applications. Two types of fungi were investigated: the mycelial form of *Aspergillus niger,* and unicellular yeast form of a species *Candida* isolated from spoiled wine. The test solutions were three commercially available disinfectants: Actisept (sodium dichloroisocyanurate: 0.25% sln., pH 5.85), Anasept (mixture of hexamethylenediamine, polyhexamethylene biguanide and quaternary ammonium compounds, 0.5% sln., pH 6.8), and Rouasan (ethanol, propan-2-ol, quaternary ammonium compounds and dodecylpropane-1,3-diamine, pH 9.25). The behaviour of the fungal cells in disinfectant solutions was assessed electrochemically to compare the response of microorganisms at biocides action, which represent the key for eliminating the contamination problems in the food industry. The experiments showed the activity of fungal cells it is possible not inhibits by some disinfectants, such Rouasan, but this disinfectant may destroits the metallic surface during the disinfection process, and damaged surface could be due to an increase attachment sites, stronger adhesion due to increased soiling/metallic surface interface areas and enhanced protection from cleaning shear forces. The surface of 304L SS was characterized by AFM, before of disinfections and after artificial. *Fig. 1* shows the modification in the number of *Candida* cells after disinfection, more than 15 hours.



a b c

Fig. 1. AFM image on SS 304L : a) without disinfectant and Candida cells: b) 1 hour Anasept disinfection and Candida cells contamination: c) 16 hour after disinfection and contamination

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FROM BIOCORROSION TO ENZYMATIC BIOFUEL CELLS POWERED BY ETHANOL AND GLUCOSE

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Corrosion of metallic materials by bacteria is a process, which involves specific biofilms and/or enzymes. Recently an increasing attention has been dedicated to biofuel cells. The main advantage of biofuel cells is that they are able to convert chemical energy into electrical energy [1]. For this conversion an enzymatic biofuel cells utilize enzymatic oxidation of such reducers as H_2, NAD(P)H, alcohols and carbohydrates at anodes and reduction of such oxidants as O_2 and H_2O_2 at cathodes. Since biofuel cells use sources of chemical energy, they can be small, and the fuel can be taken from the biological environment and even from a living organism (e.g. glucose from the blood stream), bacterium or plant [2]. The other advantages of biofuel cells are plainness in handling, simplicity of cell structure, mild conditions for operation [3] and minimized pollution in scrapping.

The most effective way for the development of enzymatic biofuel cells is to apply the enzymes that exhibit “electrical contact” with the conductive supports [4]. Redox enzymes containing heme *c* are the most promising enzymes in this context [5]. A biofuel cell, consisting of carbon rod electrodes and operating at ambient temperature in aqueous solution, at pH close to neutral was described. The constructed biofuel cell was based on heme *c* containing pyrroloquinoline quinone-dependent alcohol dehydrogenase (QH-ADH) from *Gluconobacter* sp. 33 in anode compartment and co-immobilized glucose oxidase (GOx) from *Aspergilus niger* and microperoxidase 8 (MP-8) from the horse heart in cathode compartment.

Ethanol was used as fuel of anode part and glucose as fuel of cathode part of constructed biofuel cell. Electrons extracted from ethanol during biocatalytic QH-ADH reaction were directly transferred to carbon surface. Enzymes GO*x* and MP-8 applied in the design of biofuel cell cathode were acting in consecutive mode. During GOx catalyzed glucose oxidation reaction formed hydrogen peroxide was used as substrate for MP-8 and electrons by hydrogen peroxide oxidized MP-8 were directly accepting from carbon rod electrode.

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ELECTROCODEPOSITION OF ZNFE/HYDROXYAPATITE NANOCOMPOSITES

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The preparation of composite films consisting of ultrafine hydroxyapatite (HAp) nanoparticles in a zinc–iron (ZnFe) matrix was reported. The films have been prepared by electrocodeposition from an alkaline electrolyte containing pyrophosphate as complexing agent. The HAp nanoparticles, synthesized by chemical precipitation, feature a needle-like shape with a diameter of ~10 nm and a length ~100 nm. The effects of a variety of deposition conditions, viz. current density, pH, temperature and composition of the plating bath on the codeposition of HAp nanoparticles with ZnFe-alloys were investigated by evaluating the alloy composition, nanoparticle content, structure and microhardness of the composite coatings [1]. In the plating bath, the particles bear a negative surface charge probably due to the adsorption of pyrophosphate anions. The ZnFe alloy electrodeposition, i.e. the composition of the resulting films and the cathodic current efficiency, was shown to depend upon a variety of working conditions. The incorporation of HAp nanoparticles has been determined by SEM (Fig.2) and EDX investigations. A maximum incorporation of 2.3 wt.% of HAp nanoparticles in a ZnFe matrix was achieved at 2 A dm^{-2} for 15 g l^{-1} HAp in the electrolyte. The most pronounced effect appeared due to a change in the pH and temperature of the ZnFe electrolyte (Fig.1). The incorporation of HAp nanoparticles in the alloy films increased with decreasing current density and increasing electrolyte temperature. Moreover, the nanoparticle incorporation led to an increase in the Fe content of the binary alloy and a decrease of the cathodic current efficiency. The surface morphology of the ZnFe matrix was significantly altered due to both the presence of Hap nanoparticles in the plating bath and a change in the plating conditions. Furthermore, a considerable increase in the Vickers microhardness of the films was found due to the HAp nanoparticle incorporation. Finally, the obtained results demonstrate the versatility of the electrocodeposition process as a simple and cost-effective process for the preparation of novel composite material[2].

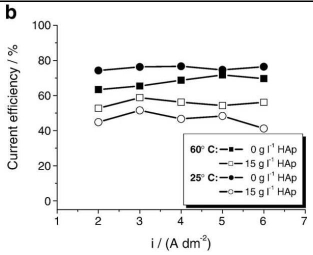

Fig. 1. Current efficiency of the ZnFe electrodeposition at pH=9.5

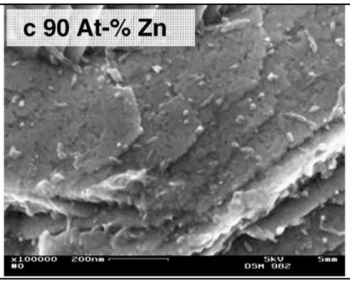

Fig.2. SEM image of ZnFe- HAp composite film plated at 5 A dm−2 and 15 g l−1 HAp in the electrolyte

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Acknowledgment: Ph.D. stud. D. Thiemig, COST D33- STSM-D33-03738(2008).

POLYURETHANE-GOLD NANOPARTICLES BIOCONJUGATES WITH ENHANCED BIOSTABILITY

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Biodegradable synthetic polymers are widely used as biomaterials because their mechanical and physical properties that can readily be adjusted by varying the preparation techniques and controlling the primary, secondary and supra-molecular structure [1]. *In vitro* and *in vivo* biocompatibility studies investigating various polyurethanes for a wide range of applications have focused on the cellular, enzymatic, and tissue responses to the material. Porous polyurethane (PU) microparticles in the size 20-60 μm based on poly(vinyl alcohol) (PVA) were synthesized by one step method under homogeneous conditions in dimethylsulfoxide solution according to our previous work [2]. Obtained microparticles are more "native-friendly" by using of biodegradable and biocompatible PVA for synthesis than that where common diols such as butanediol, hexanediol, etc. were used. However, using of PVA resulted in decrease of biostability of PU. The biostability of PU can be enhanced by incorporation of Au nanoparticles. Gold nanoparticles in PU appeared to prevent the PU from oxidation as well. Obtained PU-Au bioconjugates were successfully used for immobilization of enzymes. High catalytic activity of biocatalysts and good stability in time was observed.

Acknowledgement

The study was supported by Lithuanian State Science and Studies Foundation according to Contract No. S-12/2008.

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ALUMINIUM NICKEL ALLOYS CLADDING ON STEEL SUPPORT FOR HARD MECHANICAL REQUIREMENTS USED FOR THE BEARINGS OFFSHORE DRILLING EQUIPMENTS

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Seawater is an aggressive fluid that affects nearly all structural materials. Concomitantly with marine environment, the bearings offshore drilling equipments work under high contact pressure and variable, with poor lubrication. Not a single material can satisfy all these requirements. For this reason was proposed the bimetallic bearings for this application. At surface of the support steel was cladded by welding an aluminium bronze with nickel, manganese and iron with chemical composition determined in respect to required by work conditions, namely antifriction properties, hard mechanical properties and corrosion resistance. Weld joint characterised by three distinct zones (the cast weld zone, heat-affected zone and the parent metal) were studied. The microstructural properties of the bimetal and the behaviour to sea water corrosion were presented in this paper. The subzones developed into heat affected zone exposed to corrosive attack in sea water were also characterised. There are several differences in composition or structure that affects resistance to corrosion: in the cladding made of several layers (deposited successively by multipass welding); between filler alloy and parent metal; in the heat-affected zone adjacent to weld. In this situation a supplementary galvanic corrosion can occur. The multilayer welding technology and its parameters have been evidently studied because these also adversely affected corrosion resistance.

METAL OXIDE-HYDROXYAPATITE BIPHASIC MATERIALS STUDIED BY SEM MICROSCOPY

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In this study we present the direct observation of the micro structural evolution of mixed powders synthesized by colloidal methods from bioactive hydroxyapatite and metal oxides, in the nanoscale, prepared by wet mixing of components, before and after sintering treatment. The two component particulates having a narrow size distribution were obtained by heterogeneous precipitation method and then sintered into a bulk ceramic material. Interactions of mixed compounds consisting of hydroxyapatite and metal oxides, for creating systems with improved properties regarding biocompatibility are studied. Direct observation for some powders before and after the sintering treatment has been made by SEM microscopy. Neck formation and particles rearrangement have been observed in powder. The evolution of interfaces between particles during sintering, induced by prior compaction, is evidenced. The heating conditions were 60 and 120 minutes and the temperature was in the range from 850°C to 950°C and to1050^{o}C. It can be seen that the starting formation temperature depends on the type of the metal oxide. The results suggest that, for compacted ***powders*** the full temperature is 950°C for any metal oxide with hydroxyapatite, for a fixed holding time of 120 minutes. The morphology of the powders was observed by SEM microscopy.

The main achievements and conclusions can be drawn as follows:

(a) The metal oxide type determines micro structural evolution of mixed powder formation. The size and shape of the powders having the same composition depends on the heating temperature and the heating time.
(b) With increasing the heating time the composition' s phase will be modified from a pure metal oxide and respective hydroxyapatite, to the biphasic material composed by the mixture of the metal oxide and hydroxyapatite.
(c) Optimum heating conditions were found at the experimental testing conditions used. Future work will be focused on the usage of other metal oxides and on the characterization of their effects on the mechanical and biocompatible behaviors of the prepared compounds.

SEM STUDY FOR INTERACTION BETWEEN BIOCOMPOSITES AND CO ALLOYS

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Actually by broaden of physics-chemical link at the alloy/polymeric crown interfaces it was possible to made dental prosthetic devices for a single tooth (single crowns) with apparent improving physics-chemical and biochemical properties then the classic one.

The purpose of the present study is to evidence and to evaluate the efficiency of the alloy /ceramic and polymeric composite surface link, by SEM investigation and by measurement shear strength of the resin-alloy interface. The study's results have high lighten that the biocomposites based on HAP achieve good adhesion of the related biocomposites to cobalt alloy. Studies with electron microscopy have allowed an assessment of the quality layer adherence of ceramic and metallic oxide format. Adherence between metallic support and ceramic layer is very good throughout the entire length of support. Common to all three samples (with the submission of ceramics) is the presence of an intermediate layer between the visible metal support and ceramics submission. Layers oxide of the first two trials shows no significant differences regarding the design, quality and rugged topography. The composite's adherence to the metal is very good. In addition the appearance of an oxide layer with a different coloration and structure from the rest of the layer was observed, right next to the support, and it may have an "fastening" layer role. It was found that the direct applications of composite resins, on the surface alloy without primer using are not ensure interfacial linking of the two materials.

RADIOPACITY OF FLOWABLE RESIN COMPOSITES COMPARED WITH HUMAN TOOTH STRUCTURE

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Radiopacity is a basic requirement of restorative materials to permit its identification between the restorative material and tooth structure. The aim of this study was to analyze the radiopacity of some flowable composites and to compare with the radiopacity of enamel and dentin. For specimens were made of each flowable composites: Tetric EvoFlow (A3), Tetric EvoFlow (Bleach L), PermaFlo DC (A1, A2), Filtek Supreme XT (A3), Accolade SRO (A2), Accolade PV (A2), StarFill 2B (Dentin), StarFlow (A2), SYNERGY Nano Formula (A3.5/B3), SYNERGY Nano Formula (A4/M5), SYNERGY Nano Formula (A2/B2), SYNERGY Nano Formula (A3/D3), SYNERGY Nano Formula (Super White), els extra low shrinkage (A3), Wave (A3), wave mv (A2). The disks of samples measuring 8 mm diameter and 1 mm thickness, mesiodistally sectioned human molar 1 mm thickness and aluminum step wedges were positioned on radiographic film. Radiographs were taken with a dental X-ray (HELIODENT DS, Sirona) at 60kv, 7mA, 0.32 sec and target-film distance at 40 cm. After development, dental films were scanned for digitalization of dental radiographs and radiopacity values were recorded for every sample. The radiopacity of the samples was expressed in terms of the equivalent thickness of aluminium per 1mm unit thickness of material.

Accolade SRO (A2) and Tetric EvoFlow (A3) had radiopacity values significantly greater than enamel, while PermaFlo DC (A1, A2) and Filtek Supreme XT (A3) had close radiopacity values to enamel and lower than enamel. All materials tested had radiopacity values greater than dentin and higher than 1 mm Al. The results recorded were *different statistical* ($p = 0.5$) when was evaluated with ANOVA statistical analysis.

Conclusions: Materials tested had radiopacity values higher than 1 mm Al and were in agreement with ISO Standard 4049. Future flowable resin composites are recommended to have higher radiopacity values than dentin and perhaps ideally similar to or higher than that of enamel for improved of clinical detection. Digital image could be an alternative to transmission densitometry for evaluation of the radiopacity.

THE EFFECT OF EXPERIMENTAL BLEACHING AGENT ON DENTAL COMPOSITES

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Teeth whitening are a conservative solution when dealing with mild and moderate dental coloration. Restoration materials, especially those employed for frontal teeth, must resemble as closely as possible the hard dental tissues, which they must substitute and imitate as good as possible (and ideally be indistinguishable from them). The scope of the present study is to prepare a series of experimental dental composites and measure their color coordinates after immersion in dye solutions and after application of a whitening gel.

We have used experimental and commercial (Restacril, Nanopacryl, Compozit ligth-cured translucent, CP-AD1, CP-AD3) composite coloring tests "in vitro" were performed on samples of 30 mm diameter and 2 mm thickness, which were immersed in coffee, red wine, and two food coloring agents (red, containing Sunset yellow (E110) and carmoisine (E122), and yellow, containing Sunset Yellow, tartrazine(E102) and Ponceau 4R(E124)). The samples were subsequently removed from the solutions, rinsed with water and dried, and then measured after three days and after 2 months. On the 2 months-old samples, a whitening gel was applied (G4, 35%), and the samples were again measured after three hours and after 24 hours. Determination of colour changes. The measurements were performed with a UNICAM UV-vis spectrophotometer. From the reflexion spectrum the color coordinates (Δa^*, Δb^* ΔL^*) were determined and the color difference was calculated with the formula: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ where: ΔL^*, Δa^*, and Δb^* are changes in L^*, a^*, and b^* after bleaching.

The samples immersed in natural colorants were found to undergo a more intense coloration than those immersed in artificial colorants. The measurements showed that the samples immersed in natural dyes suffered a more intense coloration than those immersed in artificial dyes, and the effect of the 35% whitening agent was observed, values obtained after 24 hours of gel exposure are closed to the initial values measured prior to immersion in coloring agents.

BIOLOGICAL TESTS FOR NEW EXPERIMENTAL NANOCOMPOSITES

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The evaluation tests of biological response of experimental nanocomposites used in dentistry provides supplementary information related to biocompatibility of material, more specific about the effect of composites on the cellular and tissues functions. In order to describe dental nanocomposite materials, scientific research pays a lot of attention of some key factors regarding biocompatibility of materials with human body. Dental nanocomposite biocompatibility depends on the composition, localization and the interactions from mouth cavity. Nanocomposite materials determine different biological response due to the differences of composition. The aim of this study was to evaluate the biological properties of a new light-cured nanocomposite. We prepared 4 nanocomposites (NC1, NC2, NC3, NC4), by dispersing the synthesized nanoparticles ($La_2Zr_2O_7$) and glasses (glass with Ba) in the monomer mixture. The monomer mixture consists of some urethane diacrylates and dimethacrylate monomers (Bis-GMA, TEGDMA). For the biological tests of the nanocomposites we have chosen the specimen with best standard specifications. Biological tests (according to SR EN 30993-1, ISO 10993-1/1996) were carried out on 3 levels, as follows: systemic toxicology tests, irritational potential test and limited usage by intramuscular and subcutaneous implants.

To accomplish these objectives we used several groups of experimental animals, investigating systemic, local, morphological and histological effects that this material could have upon natural tissues. Biological tests demonstrated the biocompatibility of the nanocomposites. We observed a good healing without mobility or sensibility problems at the implant zone, for both subcutaneous and intramuscularly implants at 21 post implant days. For NC3 nanocomposite the histological aspect of the implant zone, revealing a small inflammatory local reaction. The evaluation of biological tests has demonstrated that the nanocomposites were well tolerated by the organism without rejection. General and local reaction has not indicated to none of the subjects that the implants have irritating, toxic and hyperplasic exaggerated compounds.

DEGREE OF CONVERSION OF SOME NEW EXPERIMENTAL DENTAL ADHESIVES

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Adhesive materials have known a very fast dynamic development, due to the new technologies in the field. In the adhesive technologies used in dentistry, the essential and critical step is the possibility to realize the adhesion of different materials to enamel and dentine.

The aim of this study was to evaluate the degree of conversion (DC) of four experimental dental adhesives (A1, A2, A1’, A2’) by FTIR spectroscopy that is a fast method to evaluate the material properties of adhesive systems. The adhesives were cured with a fast halogen light (Optilux 501) and two different light-emitting diode (Heraeus Kultzer and Ivoclar G2) at various time.

The quantity of DC has been determined as percent of the methacrylate groups originally present in the unpolymerized materials. FTIR analysis of adhesive samples after 1-week exhibit a pronounced DC (%) increase compared to the initial values for both systems. The degree of monomer conversion depends on the output and wavelength of the light, exposure time and composition of light-activated resin-based material. When applied to tooth surface, the self-etching primer acidity can be buffered by mineral content of dentin and enamel, allowing the higher monomer conversion. The changes for preparations of A2 and A2’ samples, such as reduction of the water content from Primer solution and the increase in Bis-GMA content, might have altered the adhesive material, which would modify the maximal rate of conversion and the result of the polymerization reaction of adhesive samples.

MIC IN STAINLESS STEEL PLUMBING SYSTEMS FOR DRINKING WATER

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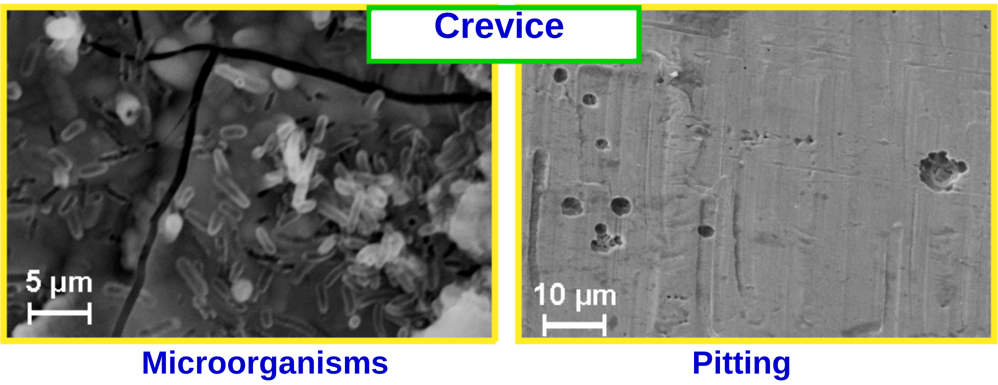
Stainless steel (SS) experiences potential ennoblement when biofilms form on its surface when contacted with sea water, brackish water or river water. Recently is has been observed that potential ennoblement is also encountered at SS in drinking water causing crevice corrosion in pressfitting joints of SS plumbing systems. However, it appeared that not all drinking waters exhibit the ability for SS ennoblement.

This case was investigated with microbiological and electrochemical methods. It was found in long term experiments with once-flow-through test rigs that biofilms are formed on SS in drinking water distribution systems and that chlorination can prevent potential ennoblement of SS in drinking waters which are active to cause SS ennoblement. Waters which generally are ineffective to promote SS ennoblement can be activated to cause ennoblement by filtering the water with carbon black. Chlorination of carbon black filtered drinking water inactivates the water again for promoting potential ennoblement.

The mechanism of this effect is discussed with respect to interphase phenomena between the SS surface and an attached biofilm. The kind of water treatment in the water works significantly influences the activity of a drinking water to cause potential ennoblement of SS in tap water. The crevice corrosion attack in pressfitting joints of plumbing systems for active drinking water can be mitigated by impregnating the O-rings in the fittings with silicone grease.



MIC at SS (1.4401) after 90 days exposure in drinking water of a big town.

ATTENDANCE LIST

ATTENDANCE LIST

Name of the meeting: COST D33 FINAL WORKSHOP
Science Officer: Dr. Erwan ARZEL
Local Organiser: Prof. Lidia BENEA, Dr. Marioara MOLDOVAN, Prof. Geta CÂRÂC

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COST - European Cooperation in Science and Technology

COST is one of the longest-running European instruments supporting cooperation among scientists and researchers across Europe. The goal of COST is to ensure that Europe holds a strong position in the field of scientific and technical research for peaceful purposes, by increasing European cooperation and interaction in this field. www.cost.esf.org

COST is an intergovernmental framework for European Cooperation in Science and Technology, allowing the coordination of nationally-funded research on a European level. COST contributes to reducing the fragmentation in European research investments and opening the European Research Area to cooperation worldwide.

The goal of COST is to ensure that Europe holds a strong position in the field of scientific and technical research for peaceful purposes, by increasing European cooperation and interaction in this field. This research initiative makes it possible for the various national facilities, institutes, universities and private industry to work jointly on a wide range of Research and Development (R&D)

COST – together with EUREKA and the EU framework programmes – is one of the three pillars of joint European research initiatives. These three complementary structures have differing areas of research.

COST has clearly shown its strength in non-competitive research, pre-normative cooperation, and solving environmental, cross-border and public utility problems. It has been successfully used to maximise European synergy and added value in research cooperation and is a useful tool to further European integration. Ease of access for institutions from non-member countries also makes COST a very interesting and successful tool for tackling topics of a truly global nature.

Nine Key Scientific Domains

As a precursor of advanced multidisciplinary research, COST plays a very important role in building a European Research Area (ERA). It anticipates and complements the activities of the EU Framework Programmes, constituting a “bridge” towards the scientific communities of emerging countries. It also increases the mobility of researchers across Europe and fosters the establishment of scientific excellence in the nine key domains:

- Biomedicine and Molecular Biosciences
- Food and Agriculture
- Forests, their Products and Services
- Materials, Physical and Nanosciences
- Chemistry and Molecular Sciences and Technologies
- Earth System Science and Environmental Management
- Information and Communication Technologies
- Transport and Urban Development
- Individuals, Societies, Cultures and Health

In addition, Trans-Domain Proposals allow for broad, multidisciplinary proposals to strike across the nine scientific domains.

What is the European Research Area?

In 2000, the EU decided to create the European Research Area (ERA). This means creating a unified area all across Europe, in which we should:

- Enable researchers to move and interact seamlessly, benefit from world-class infrastructures and work with excellent networks of research institutions;
- Share, teach, value and use knowledge effectively for social, business and policy purposes;
- Optimise and open European, national and regional research programmes in order to support the best research throughout Europe and coordinate these programmes to address major challenges together;

- Develop strong links with partners around the world so that Europe benefits from the worldwide progress of knowledge, contributes to global development and takes a leading role in international initiatives to solve global issues.

What is it for?

Such an ERA should inspire the best talents to enter research careers in Europe, incite industry to invest more in European research – contributing to the EU objective to devote 3% of GDP for research, and strongly contribute to the creation of sustainable growth and jobs.

Seven years on, the creation of ERA has become a central pillar of the EU 'Lisbon Strategy' for growth and jobs, together with the completion of the Single Market, the European 'broad-based innovation strategy' and the creation of a European Higher Education Area.

Where do we stand?

Many initiatives have been taken by the EU and Member States. But there are still strong national and institutional barriers which prevent ERA from becoming a reality.

For this reason, The European Commission has published a Green Paper on ERA reviewing progress made, where it still needs to be made and raising questions for debate. The Commission sought answers to these questions and solicited further new ideas in a public consultation which lasted from 1 May 2007 until 31 August 2007.

Following the public consultation results, the Commission and Member States are launching in 2008 new initiatives to develop ERA, including an enhanced political governance of ERA, called the "Ljubljana Process", and five initiatives on specific areas of the ERA Green Paper.

GENERAL FRAMEWORK

The main reasons for the existence of European action in the field of research and innovation are the need for a common policy, better coordination of activities, the use of research applications to benefit other policies, and promotion of the role of science in modern societies. In this light the 7th framework programme, like its predecessors, constitutes the main instrument of the European Union.

GENERAL PROVISIONS

- European Research Area: new perspectives
- European Research Area
- A broad-based innovation strategy for the EU
- An innovation-friendly, modern Europe
- Investing in research: an action plan for Europe
- State aid for research, development and innovation

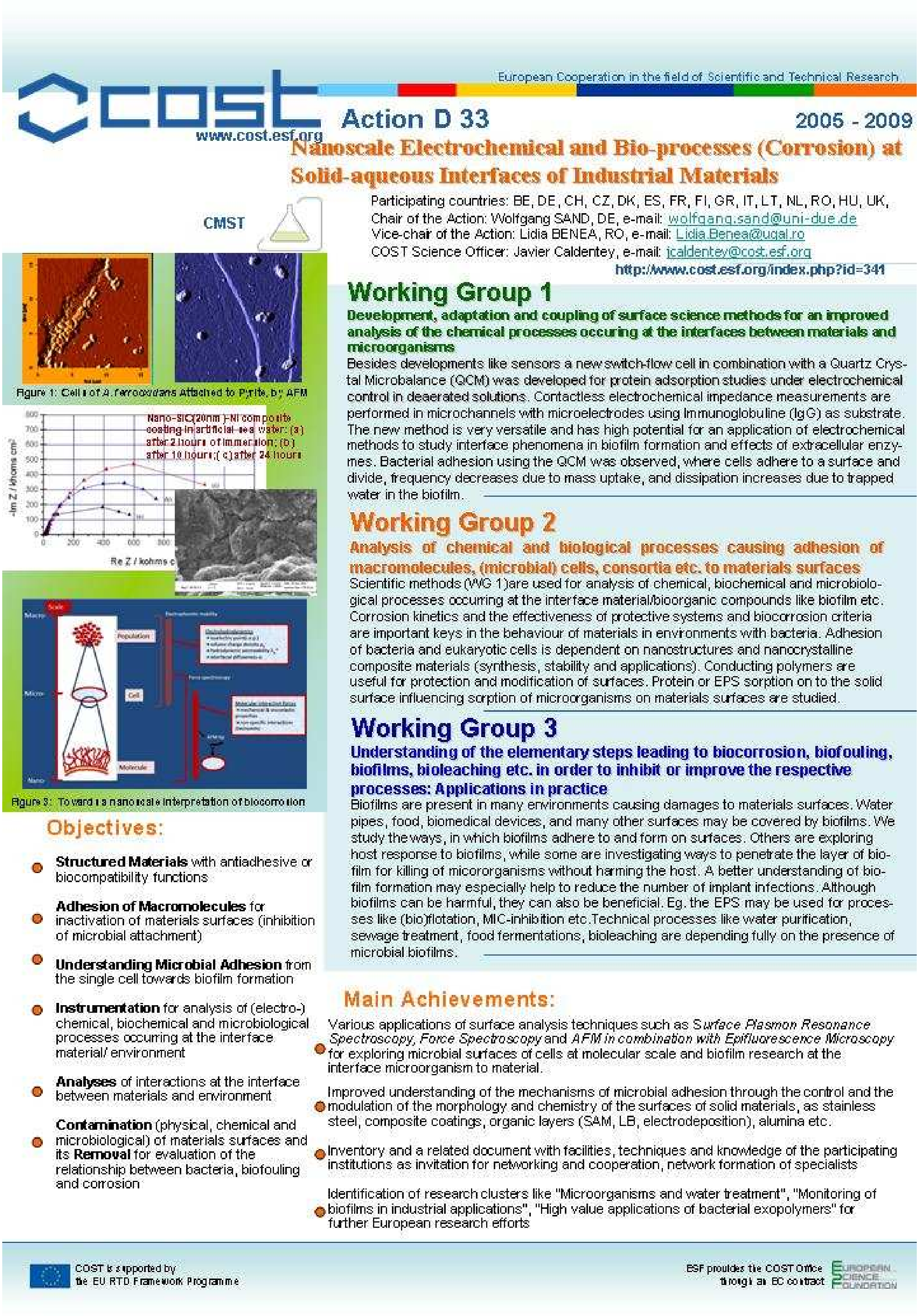
PROGRAMMES AND INITIATIVES

Seventh Framework Programme (2007 to 2013): Building the Europe of Knowledge

- Cooperation
- Ideas
- People
- Capacities
- Joint Research Centre (JRC)
- Euratom

The Sixth Framework Programme 2002-2006

- Life sciences, genomics and biotechnology for health
- Information society technologies
- Nanotechnologies and nanosciences
- Aeronautics and space
- Food quality and safety
- Sustainable development, global change and ecosystems
- Citizens and governance



European Cooperation in the field of Scientific and Technical Research

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Action D 33

2005 - 2009

Nanoscale Electrochemical and Bio-processes (Corrosion) at Solid-aqueous Interfaces of Industrial Materials

CMST

Participating countries: BE, DE, CH, CZ, DK, ES, FR, FI, GR, IT, LT, NL, RO, HU, UK,
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COST Science Officer: Javier Caldentey, e-mail: jcaldentey@cost.esf.org
http://www.cost.esf.org/index.php?id=341

Figure 1: Cells of *A. ferrooxidans* Attached to Pyrite, by AFM

Figure 3: Towards a nanoscale interpretation of biocorrosion

Objectives:

- **Structured Materials** with antiadhesive or biocompatibility functions
- **Adhesion of Macromolecules** for inactivation of materials surfaces (inhibition of microbial attachment)
- **Understanding Microbial Adhesion** from the single cell towards biofilm formation
- **Instrumentation** for analysis of (electro-) chemical, biochemical and microbiological processes occurring at the interface material/ environment
- **Analyses** of interactions at the interface between materials and environment
- **Contamination** (physical, chemical and microbiological) of materials surfaces and its **Removal** for evaluation of the relationship between bacteria, biofouling and corrosion

Working Group 1

Development, adaptation and coupling of surface science methods for an improved analysis of the chemical processes occuring at the interfaces between materials and microorganisms

Besides developments like sensors a new switch-flow cell in combination with a Quartz Crystal Microbalance (QCM) was developed for protein adsorption studies under electrochemical control in deaerated solutions. Contactless electrochemical impedance measurements are performed in microchannels with microelectrodes using Immunoglobuline (IgG) as substrate. The new method is very versatile and has high potential for an application of electrochemical methods to study interface phenomena in biofilm formation and effects of extracellular enzymes. Bacterial adhesion using the QCM was observed, where cells adhere to a surface and divide, frequency decreases due to mass uptake, and dissipation increases due to trapped water in the biofilm.

Working Group 2

Analysis of chemical and biological processes causing adhesion of macromolecules, (microbial) cells, consortia etc. to materials surfaces

Scientific methods (WG 1)are used for analysis of chemical, biochemical and microbiological processes occurring at the interface material/bioorganic compounds like biofilm etc. Corrosion kinetics and the effectiveness of protective systems and biocorrosion criteria are important keys in the behaviour of materials in environments with bacteria. Adhesion of bacteria and eukaryotic cells is dependent on nanostructures and nanocrystalline composite materials (synthesis, stability and applications). Conducting polymers are useful for protection and modification of surfaces. Protein or EPS sorption on to the solid surface influencing sorption of microorganisms on materials surfaces are studied.

Working Group 3

Understanding of the elementary steps leading to biocorrosion, biofouling, biofilms, bioleaching etc. in order to inhibit or improve the respective processes: Applications in practice

Biofilms are present in many environments causing damages to materials surfaces. Water pipes, food, biomedical devices, and many other surfaces may be covered by biofilms. We study the ways, in which biofilms adhere to and form on surfaces. Others are exploring host response to biofilms, while some are investigating ways to penetrate the layer of biofilm for killing of micororganisms without harming the host. A better understanding of biofilm formation may especially help to reduce the number of implant infections. Although biofilms can be harmful, they can also be beneficial. Eg. the EPS may be used for processes like (bio)flotation, MIC-inhibition etc.Technical processes like water purification, sewage treatment, food fermentations, bioleaching are depending fully on the presence of microbial biofilms.

Main Achievements:

- Various applications of surface analysis techniques such as *Surface Plasmon Resonance Spectroscopy, Force Spectroscopy* and *AFM in combination with Epifluorescence Microscopy* for exploring microbial surfaces of cells at molecular scale and biofilm research at the interface microorganism to material.
- Improved understanding of the mechanisms of microbial adhesion through the control and the modulation of the morphology and chemistry of the surfaces of solid materials, as stainless steel, composite coatings, organic layers (SAM, LB, electrodeposition), alumina etc.
- Inventory and a related document with facilities, techniques and knowledge of the participating institutions as invitation for networking and cooperation, network formation of specialists
- Identification of research clusters like "Microorganisms and water treatment", "Monitoring of biofilms in industrial applications", "High value applications of bacterial exopolymers" for further European research efforts

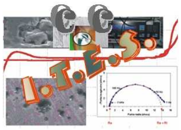
COST is supported by
the EU RTD Framework Programme

ESF provides the COST Office
through an EC contract
European Science Foundation

Dunărea de Jos University of Galati

The **University " Dunarea de Jos " of Galati (UDJG)** was founded in July, 1974 by merging the Polytechnical Institute and the College of Education. The Polytechnical Institute of Galati had at its origins the Naval and Mechanical Engineering Institute wich has been founded in 1951. In 1953, the Institute of Fish Breeding and Fishing Technology located in the city of Constanta merged with the Naval Institute of Galati under the name of Technical Institute of Galati.
The University of Galati organises programs for the doctoral degree and master degree in the technical fields of materials science, chemistry, physiscs, mathematics, economy, food technology and fishing, automatic control and computation techniques, artificial intelligence. The University of Galati is also providing programs for the doctoral degree in the field of social and humanistic sciences.
16 Faculties. 18000 Students. 82 Specialisations. Site web: www.ugal.ro

Competences Center: Interfaces-Tribocorrosion and Electrochemical Systems (CC-ITES)



Research Center CC-ITES is founded and authorized in 2007 as Competences Center in the field of interfaces, tribocorrosion and electrochemical systems. It is a multidisciplinary research group with the base members in the **Faculty of Metallurgy and Materials Science** and **Department of Chemistry from the Faculty of Sciences.**

Web: http://www.fmet.ugal.ro/CC_ITES/INDEX.htm

CC-ITES: EXPERTISE AND COMPETENCES
Fundamental and Applied Research

Chemistry
-Electrochemical studies and methods. Chemical technologies. Surface Chemistry.
-Corrosion and wear corrosion (tribocorrosion) of materials (mechanisms and kinetics).
-Fundamentals of Metal Electrodeposition,
-Mico and Nano Structued Composite Coatings.
-Research on surface modifications technologies to improve the corrosion and wear resistance of materials.
-Research on environment compatibility of triboreactive materials and lubricants.
-Development and understating of surface reactivity.
-Research on lubricants and additives.
-Electro analytical methods of investigations.
-Kinetic and mechanism of materials (metallic, coatings) degradation by combined action of corrosion and wear = tribocorrosion.

Materials Engineering
-Nano and micro structured composite coatings, complex degradation, biomaterials passive state, corrosion, kinetic, tribocorrosion
-Surface treatments by electrodeposition of metals, alloys and composites to improve the corrosion and wear resistance of materials.
-Corrosion and wear corrosion, Tribocorrosion of materials.
-New materials obtained by co-deposition of dispersed particles with metals and alloys to obtain micro and nano structured coatings.
-Nanomaterials.
-Electrocatalytic activity of metal matrix composite coatings obtained by electro-co-deposition.
-General and Inorganic Chemistry.
-Industrial Wastewater treatments.
-Resin-modified glass ionomer restorative materials for tooth structures.
-Nano and microstructuration.

Materials characterisation:

-DC and AC electrochemical measurements,
-Scanning electronic microscope,
-Transmission electronic microscope,
-X-ray disperse analysis,
-2D -3D surface micro topography and surface analysis

EDUCATION:

➤**Engineering studies:**
-Materials Science.
-Environmental Engineering.

➤**Master studies:**
-Nanotechnologies and Multifunctional Materials.
-Advanced Materials.

➤**Doctoral studies:**
-Materials Engineering.

▶**Collaborators (Teaching and Research):**

- ●Ecole Centrale Paris, France. Laboratoire Génie des Procédés et Matériaux (LGPM).
- ●Katholieke Universiteit Leuven – Belgia. Chemical Division – Department Metallurgy and Materials Engineering.
- ●University of Duisburg Essen, Biofilm Centre, Aquatic Biotechnology, Duisburg, Germany.
- ● STN lab Department of Physics & Deparment of Biology University of L'Aquila, Italy.
- ●Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris, Paris, France.
- ●Laboratoire Interfaces et Systèmes Electrochimiques, UPR 15 du CNRS, Casier 133, Université Pierre et Marie Curie, Paris. France.
- ●University of Minho, Centre for Mechanics and Materials, Research Group on Functionalized Materials and Surfaces Performance. Portugal.
- ●Politecnico di Milano, Italy.

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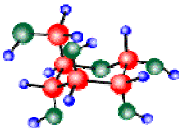
Babeş-Bolyai University Cluj – Napoca

Raluca Ripan Chemistry Research Institute



The **Babeş-Bolyai University** (UBB - Universitatea Babeş-Bolyai) in Cluj-Napoca is the largest university in Romania. With almost 50,000 students, the university offers 105 specialisations, of which there are 98 in Romanian, 52 in Hungarian, 13 in German, and 4 in English. The university was named after two prominent Transylvanian scientists, the Romanian scientist Victor Babeş and the Hungarian mathematician János Bolyai.

Composite Materials Department

KEY COMPETENCES AND SKILLS WITHIN THE ORGANIZATION

- synthesis of nanoparticles, bioglasses and ceramics
- surface treatments of different nanoparticles
- synthesis of monomers with low polymerization shrinkage
- structural and chemical characterization of inorganic particles, monomers
- self-curing and light-curing composites used in medicine, electronics and other applications
- fiber-reinforced composites with improved flexural strength, modulus of elasticity, toughness
- new technologies for obtaining the composite materials
- structural and physical- chemical characterization of the composites
- mechanical tests for composite materials investigation of interface processes to establish the interactions between cells and biocomposites

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S.C. OC SOLUTIONS S.R.L.

The main objective is consultancy at high professional, to develop an efficiently communication, fast and benefit between researchers and companies.

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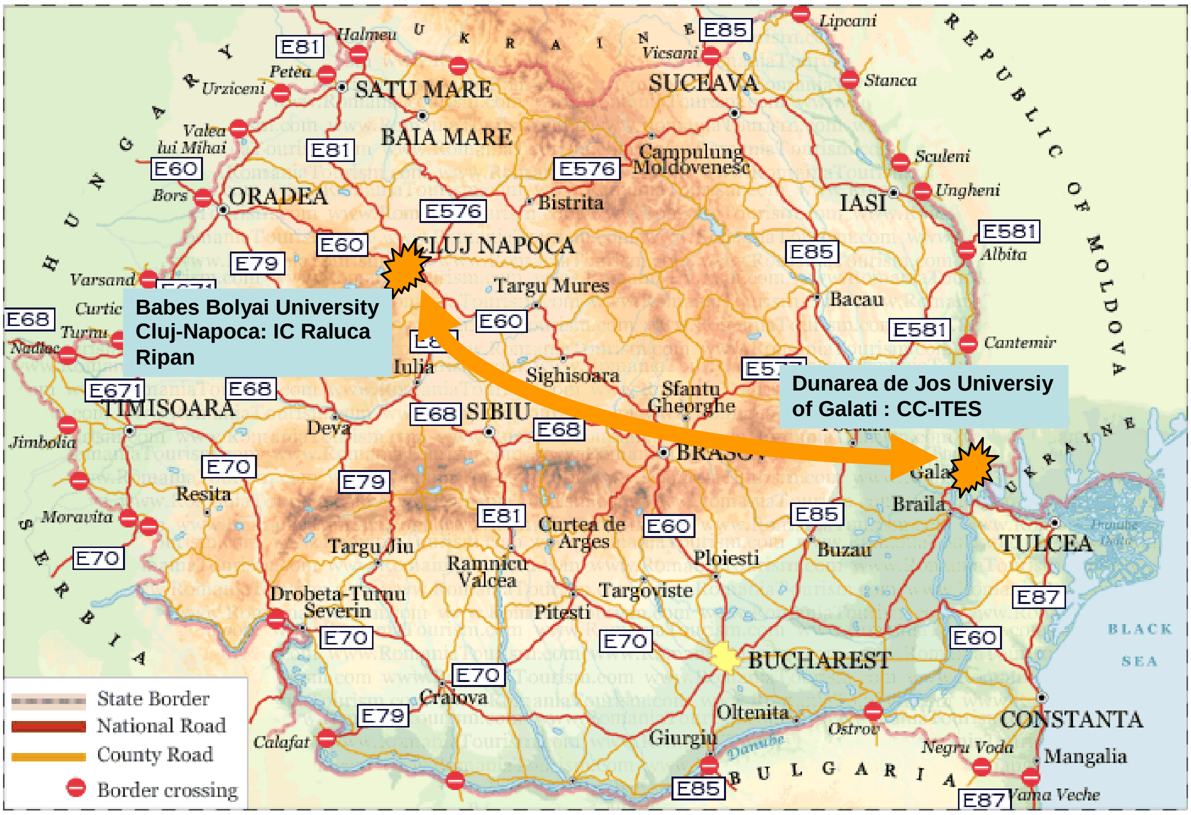
E-mail: info@ocsolutions.eu

Map of ROMANIA



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Dunarea de Jos Universiy of Galati : CC-ITES

Notes

ISBN 978-973-1937-09-0