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Scientific Cooperation
between the Institute of Atomic Physics (IFA), Romania
and the Alternative Energies and Atomic Energy Commission (CEA), France



Activity Report on 2011

Bucharest-Magurele, ROMANIA
2012

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Brief overview of IFA & CEA



The Institute of Atomic Physics (IFA) located at Magurele was established in 1956. It spun off from the Institute of Physics of the Romanian Academy founded in 1949 under the leadership of the eminent scientist Horia Hulubei who was also the first director of IFA.

IFA laid the foundations of a Romanian scientific research elite and a renowned scientific research school: IFA is the cradle of the Romanian physics. The development of the Physics Platform located at Magurele reached its peak in the 1970s bringing together a human potential and a research, educational, even a social infrastructure impressive for that time. The science performed at Magurele became widely acknowledged by the international scientific community, setting a high standard for the Romanian scientific research.

In December 2008, IFA was reorganized by government decision with the view to playing a new and enhanced role in the development of the Romanian physics research.

Following its reorganization, IFA's main achievements comprise:

- Research Unit of the Romanian EURATOM-Fusion Association (since 1999)

Since 1999 when the Contract of Association with EURATOM was signed, the Institute of Atomic Physics has coordinated the participation of Romania in the European integrated scientific research in controlled thermonuclear fusion.

- Cooperation agreement with CEA (since 2009)
- Evaluation and Strategy of the Romanian physics - ESFRO project (2009-2011)
- Executive Agency for the F4E-RO Programme (since 2010)

The Institute of Atomic Physics was designated by the National Authority for Scientific Research as the executive agency for financing, in the frame of F4E-RO programme, the projects obtained by the Romanian institutions following the calls of European Fusion for Energy Agency.

- Management of the CERN-RO Programme (since 2011)

The Institute of Atomic Physics was appointed by Government decision, to ensure the management of the participation of Romanian institutions in CERN's programmes and scientific projects.

IFA pursues a pro-active agenda for providing a stimulating scientific policy for the development of the Romanian physics research and to increasing the visibility and impact of physics in our society.



Brief overview of IFA & CEA

The CEA, the French Alternative Energies and Atomic Energy Commission (Commissariat à l'énergie atomique et aux énergies alternatives), is a public body established in October 1945 by General de Gaulle.

The CEA is based in ten research centers in France, each specializing in specific fields. The laboratories are located in the Paris region, the Rhône-Alpes, the Rhône valley, the Provence-Alpes-Côte d'Azur region, Aquitaine, Central France and Burgundy. The CEA benefits from both the strong regional identities of these laboratories and the partnerships forged with other research centers, local authorities and universities.

The CEA leads research, development and innovation in the following fields: low-carbon energies, defense and security, information technologies and health technologies. It conducts also fundamental and applied research into many other areas, including the design of nuclear reactors, the manufacturing of integrated circuits, the use of radionuclides for curing illnesses, seismology and tsunami propagation, the safety of computerized systems, etc. It has one of the top 10 supercomputers in the world, the *Tera-100*.

Regarding the scientific and technical collaboration agreements, CEA negotiates and implements scientific and technical cooperation agreements with foreign organizations from USA, Brazil, Morocco, Tunisia, Russia, India, China, Vietnam, Korea and Japan in both nuclear and non-nuclear fields.

The CEA is a technological research body which has developed extensive expertise in a number of fields – energy, information and health technologies and nanotechnologies, in particular – which are now central to the subjects studied within the European Research Area. The CEA implements an extremely proactive policy regarding the collaboration with its European partners, which is manifested in its highly-committed involvement in a series of research and development framework programmes (FP). In this respect, it is noteworthy to mention that the CEA is currently involved in more than 180 projects.

The CEA plays a significant role in human resources and training throughout Europe, promoting professional development opportunities for researchers and students.

General Agreement for Scientific Cooperation between IFA and CEA

Strengthening the scientific cooperation between France and Romania in the field of physics is an initiative designed to reinforce the importance of scientific dialogue and knowledge transfer as a base for developing a common pool of scientific knowledge and enhancing the competitiveness in this area of research.

The signing of the General Agreement for Scientific Cooperation between CEA and IFA, on December the 2nd, 2009, was a step envisaged in the Road Map for the Strategic Partnership on science and technology between Romania and France established in 2008.

The two institutions were represented by Florin Dorian Buzatu - IFA Director General and Hervé Bernard - CEA vicepresident. The event was also attended by Mr. Gerard Cognet, CEA Director for Eastern Europe and Mr. Marius Enachescu, vice-president of the National Authority for Scientific Research.

The **fields of cooperation** are:

- **Nuclear Energy**: nuclear safety, development of new generation nuclear power reactors, spent fuel and radioactive waste management, exchange information relating to nuclear energy, education and training;
- **New Technologies for Energy**: fuel cells, solar cells, energy storage, hydrogen;
- **Fundamental research on Energy**: nuclear fusion and fission, matter sciences, climate sciences;
- **Technologies for Information and Health**: micro and nanotechnologies; software technologies, biotechnologies, radiobiology and nuclear toxicology, radioprotection and medical imaging.

Following the two calls launched on 3rd May, 2010 and 3rd October, 2011 for research projects proposed by the Romanian institution together with units of the CEA, the first of its kind in the recently established partnership between IFA and CEA, a total of 17 joint research and development projects are currently funded. The projects will run for three years and will benefit from mixed financing provided equally by the National Authority for Scientific Research and CEA, respectively.



Signing the Cooperation Agreement, December 2nd, 2009

Photosensitive Azopolymers for Biological Applications



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The project aims at the synthesis and characterization of «smart» polymers for biological applications, sensitive to external light stimuli. The study of supramolecular reorganization processes of azo-polymer systems, induced by UV-VIS laser radiation is one of the main objectives of the research. The material reordering phenomena are connected with the trans-cis photo-isomerization capability of the azobenzene groups present in the polymeric side chain. The surface patterning of films in the optical wavelength scale when excitation is performed with an intensity pattern is one of the most interesting effects of this trans-cis photo-isomerization process. Another possibility to exploit the azo-polymers capability to interact with the light is the synthesis of the amphiphilic systems. In this case, the photo-isomerization process in an aqueous medium may induce aggregation/disaggregation phenomena, leading to the formation of photosensitive micelles.

There are several possibilities to use the azopolymers in the biological field, and the project will be focusing on the following: obtention of nanostructured films as support for directional cell cultures; nano-optical (laser) manipulation of biomolecules immobilized on the surface of azo-polymeric films; the study of the photosensitive amphiphilic systems with potential application in the controlled release of drugs. The main stages of the project implementation: **2010** - Azo-polymers synthesis and characterization; **2011** - Surface relief grating formation in different laser irradiation conditions; **2012** - Nano-structuration of the azo-polymers associates and the cytotoxicity preliminary tests of the obtained materials; **2013** - Laser nano-manipulation of the biomolecules on the surface of different azo-polymeric films.

In agreement with the objectives assumed for 2010-2011, firstly we synthesized and characterized a large class of polysiloxanes modified with different azo-groups (azobenzene, CF₃-azobenzene, CN-azobenzene, azonaphthalene), donor/acceptor groups and nucleobases. The capacity to obtain nanostructured films having an imposed surface geometry was investigated, using continuous [1, 6, 7] or pulsed laser sources. The possibility to obtain nanostructured surfaces containing gratings or pillars with different heights and periodicity was demonstrated (Fig.1). Function of the chemical structure, the film surface relief can be stable (more than 90 days), or unstable (erasing 20-90 min after the interruption of the laser irradiation source). Using a pulsed laser source nanostructured surfaces can be also obtained, but the relief quality is not as good as in the case of continuous laser irradiation. The relationship between the cells and the extracellular matrix (ECM) is dynamic and reciprocal, changing with cellular differentiation or tissue remodeling. This interplay has become a dominant theme of basic biomedical research within the last years. As a consequence the influences of the surface chemical signals and geometric characteristics of the azo-polymeric films on the cell adherence capacity and cell development were investigated [6].

As concerns the amphiphilic azo-polymers, their capacity to generate photosensitive micelles which are capable to disaggregate under UV irradiation was demonstrated [2]. As a consequence of the very particular architecture of the azo-polysiloxane (having both hydrophilic and hydrophobic groups connected to the same chain) micelles with amphiphilic surfaces were

obtained. Molecular modeling studies confirmed the existence of the amphiphilic surface corresponding to the micellar aggregate [3]. As a function of the polymer chemical structure, photo-sensitive inter-micellar clusters or vesicles can be obtained with potential applications in drug delivery systems.

Taking into consideration all the results obtained until now, the joint research developed by the Romanian and French teams have high chances of being continued and extended. At this moment the research teams prepare the documentation for a FP 7 European project (coordinated by CEA) which supposes the implication of other three research groups from 6 universities from Paris (France), Ecole Polytechnique Fedrale de Lausanne (Suisse) and the Institute of Biochemistry of the Romanian Academy (Romania).

As one can see in Fig. 2 nano-structured surfaces can be prepared thus increasing by 2 or 3 times the rate of cell division, or their apoptosis (cell death).

The possibility to obtain photo- [2] or thermo-sensitive [3, 4] micelles was investigated, too. The micellar systems were evaluated from the point of view of the critical concentration of the aggregation, micelles diameters and aggregation/disaggregation capacity as a result of the interaction with external stimuli (light or temperature). These polymers have potential applications in the field of drug delivery systems. The aggregation/disaggregation micelles capacity was also investigated, using molecular simulation (molecular dynamics). The theoretical studies were in a very good agreement with the experimental results.

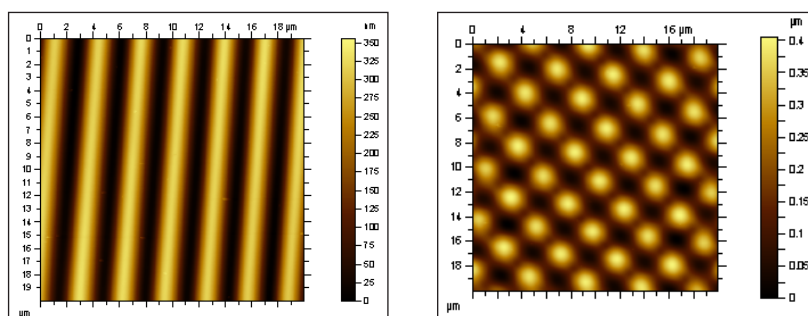


Fig. 1. AFM images of azo-polysiloxanic films having gratings (left) or pillars (right)

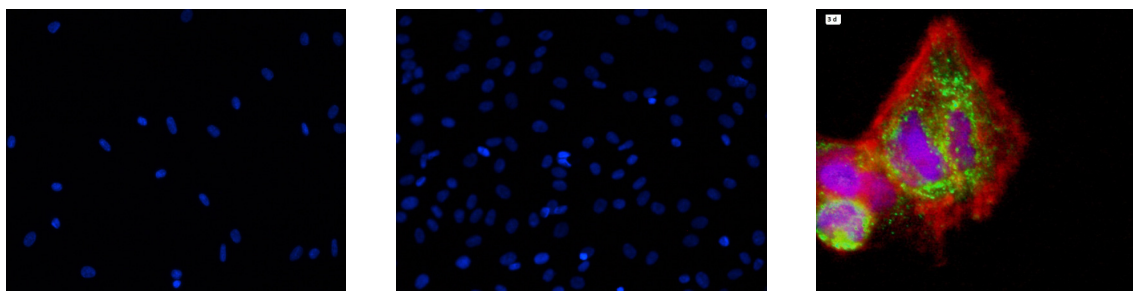


Fig. 2. Immunofluorescence microscopy images showing the cell nuclei on the plane (left) and structured (middle) azo-polymeric film; or cellular aberration (right)

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Study of the influence of forced and natural convection on impurity segregation and coating stability in the ingot growth of multicrystalline Silicon for photovoltaic applications



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It is well-known that melt convection play an important role in the impurities distribution and segregation in the ingot growth of multicrystalline Silicon for photovoltaic applications. Therefore one of the objectives of the project is to study the influence of natural convection on impurity segregation and coating stability. In order to ensure a better control of the crystal quality, it is necessary to propose new methods allowing to tailor the convection within the solidifying melt adapted to the crystal growth of large scale silicon ingots. The objective of the present project is thus to focus on these issues by studying stirring devices based on the use of rotating blades. The problem will be addressed using both numerical simulation and experiments.

The specific objectives are:

Objective 1: *Experimental and numerical study of natural convection effect on impurity segregation and coating stability in a Bridgman method for multicrystalline Si growth.*

Because of moderate costs (small crucible diameter-max 3cm), the Bridgman equipment from Crystal Growth Laboratory (Fig.1), Faculty of Physics, West University of Timisoara is ideal for a parametrical study. Impurities distribution will be investigated for different growth parameters. Experimental results (temperature and concentrations) will be compared with numerical results in order to validate numerical models. First multicrystalline silicon ingots obtained in Bridgman equipment are presented in Fig.2.

Objective 2: *Modelling of Si crystal growth process in furnaces with stirring devices.*

Numerical simulation will be performed for the experimental configurations of the INES furnaces in order to understand the physical phenomena and to give information for the design of the experimental configuration. Time-dependent computations will be carried out with the software STHAMAS3D, which was developed at the Crystal Growth Laboratory in Erlangen, under the coordination of Prof. Dr. D. Vizman and already validated by experiments for the Czochralski and Bridgman processes. The first results on modelling of dissolution rate were accepted for publication in Int. J. of Heat and Mass Transfer (Numerical study of the melt convection on the crucible dissolution rate in a silicon directional solidification process, A.Popescu, D. Vizman)

Objective 3: *Growth of multicrystalline silicon with a stirring device in laboratory and pilot scale furnaces.*

Experimental work will be initiated in a laboratory scale (2 kg ingots) furnace at INES. The laboratory furnace features cylindrical crucibles of appr. 15 cm in diameter. A single rotating blade will be implemented on the crucible axis. The first point to be verified is whether the induced flow damages the Si_3N_4 coating, and whether the results of the release of particles within the melt and/or increased infiltration of liquid Si into the coating are due to a possibly increased de-oxidation rate.

During the first year of the project both experimental and numerical investigations were performed.

From the experimental point of view, using a Bridgman equipment multicrystalline silicon crystals (Fig.2) were obtained for various temperature gradients and growth rates. It resulted that the grain structure and the interface shape are strongly dependent on the growth parameters.



Fig.1. First page Crystal Growth and Design



Fig.2. Multicrystalline silicon ingots obtained by Bridgman method

Using numerical simulation, the influence of melt convection on the crucible dissolution rate in a silicon directional solidification process was studied. It was found that convection speeds up the impurities transport from the crucible wall into the melt and increases the crucible dissolution rate. Numerical simulations show that the effect of convection on impurities transport and crucible dissolution rate is much stronger for higher values of diffusion coefficient. The results were published in Int. J. Heat and Mass Transfer [1] (IF: 1.89). Numerical simulations were also carried out to investigate the influence of the liquid phase temperature gradient and growth rate on the melt convection and S-L interface shape in a pilot configuration for unidirectional solidification of multicrystalline silicon. The results of 3D local simulation showed that the melt convection and interface shape strongly depend on the temperature gradient in melt and on the growth rate. It was found that by increasing the temperature gradient in the melt the regularity of the flow patterns in the melt increases. The influence of the growth rate is somehow similar, the regularity of the flow patterns increases with the increase of the growth rate. These results were published in Crystal Growth and Design [2] (IF: 4.39). It is also important to mention that the cover page of the January issue contain our results (see Fig.1.).

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Project webpage address: http://www.physics.uvt.ro/~vizman/CONSIL_web_page/

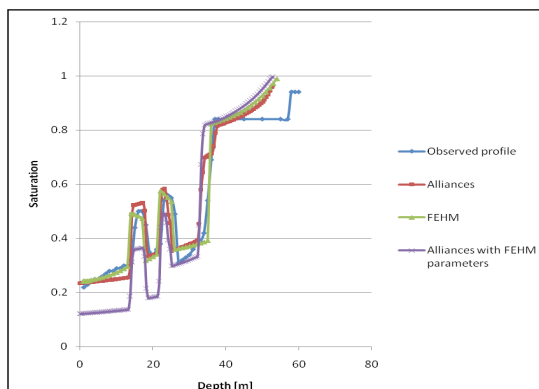


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The NSRAWD project – performing between 2010 and 2013 – sets itself to establish a collaboration between INR and CEA in the field of numerical simulations for radioactive waste disposal, by combining modeling activities with experimental tasks in order to improve and validate numerical models used to simulate water flow and contaminant transport. The numerical model appropriate for each element of the disposal system will be coupled in Alliances platform for being further applied in the integrated safety and performance assessments of the conceptual LILW repository to be built at Saligny site. The project aims to capitalize on both the wide experience of CEA specialists in developing numerical models and the capabilities of INR to perform on site tests and to work with computer codes.



Output of FEHM and Alliances for the saturation profile relative to the experimental profile

In 2011, the CAST3M code in the Alliance platform developed by CEA, ANDRA and EDF and licensed to INR in 2010 in the framework of the project was used by INR specialists to produce the water flow model for unsaturated area of the Saligny site. Water flow and tracer transport (iodine) through unsaturated area of the Saligny site have been also simulated with FEHM. Most often, water flow modeling in unsaturated area is done in steady state conditions, by considering that, on long term, seasonal variations have no impact on radionuclide transport. For Saligny, computational models have indicated that the impact of hydrologic regime variations is not felt below 5 m, the fact being confirmed by on site measurements.

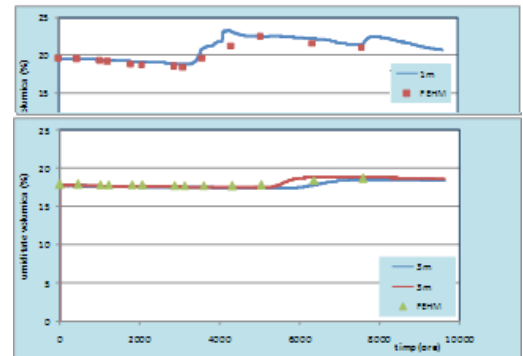
The estimations of the steady state water flow in unsaturated area performed with FEHM and CAST3M codes were compared with a moisture profile obtained by laboratory investigations on samples taken from drillings or by on site measurements. The results showed that the use of the same van Genuchten parameters in Alliances and FEHM leads to an underestimation of the saturation profile by CAST3M. The parameters needed for saturation law implemented in CAST3M code were obtained from experimental suction curves so as to optimally correspond to the average of saturation and pressure values in each layer. The result obtained in this case presents a very good correlation with the experimental profile. A water flow simulation in transient conditions with FEHM code was also performed, the purpose of this model coming from the need to validate contaminant transport in an unsaturated geological environment near the earth surface, based on a tracer test accomplished in this year. A time variant boundary condition was used at the upper part of the computation domain, derived from the existent run-off regime and moisture data registered during October 2009 and October 2010, allowing estimation of evapotranspiration rate and soil water inflow. The 2D mesh of unsaturated area covers a representative length of 100 and contains 7 distinct layers corresponding to the geological units and subunits of the disposal area, lying between 10 and 65 mDMN. The stratigraphic model was developed based on lithologic data obtained from geological investigations. The physical and hydrogeological characteristics of each layer were determined based on experimental data

collected in the framework of a site characterization programme developed in INR between 1996 and 2000. A very good correlation can be observed by comparing the computed values obtained with on site measurements, for all considered depths. The model simulates with great accuracy the decrease in soil water content due to evapotranspiration, both during warm and cold period of the year.

For depths of 1 m and respectively 3 m, FEHM also estimates very well the increase in moisture, of both the value of water content and the kinetics variation. The values are less close to each other in case of 0.5 m and 2 m depths where the predictions indicated that the kinetic for variation of pore water content is slower than that obtained from on site measurements.

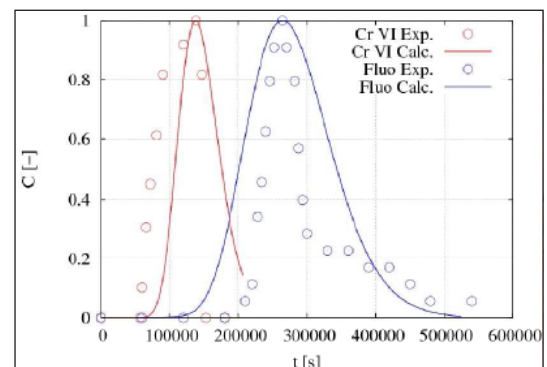
The INR team involved in the project together with a CEA specialist designed, planned and implemented an experimental program, namely a tracer test, designed to monitoring the transport of chemical species in transient regime in the unsaturated area. The test targets especially assess the sorption kinetics and equations, transport parameters, longitudinal and transversal dispersion coefficients to be used in the computational model. Kalium iodide was used as a tracer based on several criteria such as relevance for assessing the radiological impact, environmental impact, existence of a similar isotope lacking radioactivity, the possibility of detecting it through analytical methods. The concentration of tracer solution was computed taking into account the natural concentration of iodine in the geological environment and the detection limits of the methods that will be used to determine the tracer distribution at different times and depths. The selected analytical method to determine iodine in pore water is ICP-MS that allows measurements of concentrations up to 10-12 g/L. The experimental program was supplemented with the acquisition of new data specific to Saligny site that are needed for validating the flow and transport models. Iodine transport was modeled with FEHM, starting from water flow simulations. The source term was introduced as a step function that simulates the launching of the entire tracer solution in 5 minutes (the time needed for the entire kalium iodide solution to be absorbed on loess until reaching a saturation on a distance of 20 cm). The nodes for the model associated to the launching test were chosen at 0.6 m and 0.7 m depths from the surface, in the median zone. The iodine concentration in the source term was equal to the concentration in the tracer solution (20 mg/L). Although in Saligny geologic environment there is a natural iodine concentration, in the initial conditions of the model this concentration was neglected. With these assumptions, FEHM predictions on iodine transport in unsaturated area in transient conditions indicate a relative fast migration of tracer mainly on vertical direction. The ascendant flow due to evapotranspiration significantly contributes to iodine transport towards the surface, leading to concentrations with 3 orders of magnitude lower than in the launching point after only 22 days. The water from run-off dilutes the tracer and transports it in the downward flow, flattening the concentration profile and reducing the concentration in the launching area with 1 order of magnitude after 129 days and with 2 orders of magnitude after 222 days. The lateral tracer migration due to the dispersive term from the transport equation is estimated by FEHM simulations at maximum 2 m for the time interval considered (365 days). The predictions may be affected by the discretization of 1m in horizontal plan but also by the lateral dispersion coefficients used for loess. The values will be improved after the experimental results of the tracer test are available.

The activities dedicated to saturated area of the Saligny site focused on the simulation of tracer dispersion in the aquifer using the Alliances platform and were performed by the CEA team. A comparison of the results with the output of the model implemented in FEHM by INR was also accomplished.



FEHM computation versus on site measurements of soil water content for depth of 1m (top) and 3m (bottom)

Tracers breakthrough curves - Alliances predictions vs. experimental data





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Iron monosulfides (FeS) are stable at low redox potential (Eh) and proton concentration ([H+]). When Eh and [H+] increase, FeS minerals are decomposed, releasing the toxic elements incorporated in their matrix (Pb, Cd, Hg, Cu, As etc.) and sulfur species with reducing properties

$$\text{FeS} + 1/4[2+2y/x-z/x-p/x]\text{O}_2 + [z/2x+p/2x-1]\text{H}_2\text{O} = \text{Fe}^{2+} + 1/x\text{H}_z\text{S}_x\text{O}_y^{\text{p-}} + [p/x-2]\text{H}^+$$
where the oxidation state of sulfur in $\text{H}_z\text{S}_x\text{O}_y^{\text{p-}}$ is between -II and +V. These latter species buffer the redox properties of the dissolution medium and may alter the migration of redox-sensitive stable elements (like soluble Cr(VI)) and radionuclides (like soluble U(VI), Tc(VII) or Np(V)) out of polluted sites by promoting the reducing and precipitation.

Project objectives

Taking into account the above mentioned issues, an accurate knowledge of the kinetics and mechanisms of sulfur-bearing species release during FeS dissolution is ensured. The focus of both research teams was and will be on the: (1) investigation of FeS dissolution reactions by various electrochemical techniques, (2) characterization of solid reaction products formed on surface of FeS electrodes using surface science techniques, (3) identification of the main factors controlling FeS dissolution, and (4) development of theoretical models to estimate the redox buffer potential of FeS.

Obtained results

During the first year of research the oxidative dissolution of FeS in the presence of dissolved oxygen has been studied using aqueous batch experiments [1,2], electrochemical [3,4] and spectroscopic studies [1]. Electrochemical experiments were carried out in a conventional three-electrodes electrochemical cell with a Pt counter electrode and saturated calomel reference electrode (Figure 1).

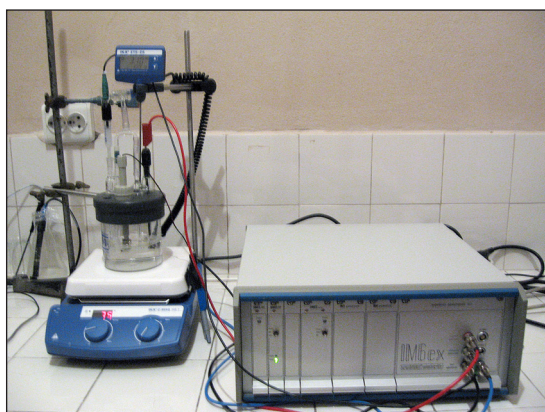


Figure 1. Equipment used to investigate electrochemical dissolution of FeS.

The electrochemical parameters (exchange currents densities, charge transfer resistances, etc) of FeS oxidative dissolution in air-saturated solutions were measured as a function of pH and temperature (Figure 2).

The reaction order with respect to $[H^+]$ is 0.7 at 30°C, and activation energy is 24.5 kJ mol⁻¹ (initial pH 2.5). The values obtained for the kinetic parameters suggest that the FeS oxidative dissolution is controlled by the diffusion of reaction participants across an obstructive layer (sulfur rich layer at high $[H^+]$ or a layer enriched in Fe(III)-O-H species at low $[H^+]$) formed on mineral surface. This reaction pathway is in good agreement with the results obtained during aqueous batch experiments [1,2]. By comparing the reactivity of FeS to pyrite in similar experimental conditions it was found that FeS has a higher oxidation rate than that of pyrite [4].

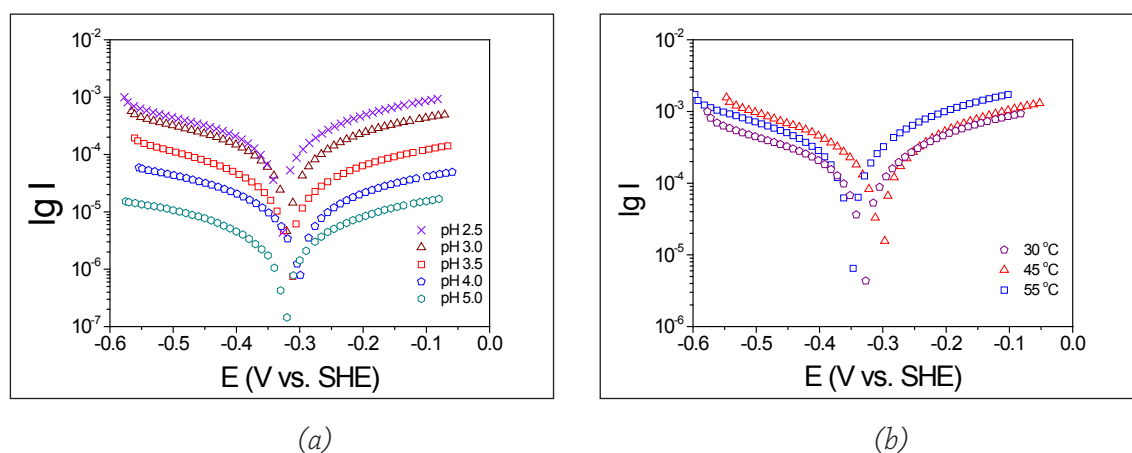


Figure 2. Potentiodynamic polarization behavior of FeS in contact with HCl solutions at 30°C (a) and initial pH 2.5 (b).

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The general objective of the project is to obtain metal particulates and powders, with fine control of their properties (size, surface chemistry, structure) and their transformation by using innovative plasma and laser methods in order to insure safer manoeuvrability with respect to nuclear safety issues. The general objective incorporates a series of particular objectives, as follows:

1. The investigation of laser ablation for fabrication of nano/microparticles of Al, Mg and W in gas and liquid phase;
2. Fabrication of composites consisting of carbon or hydrogenated carbon matrix incorporating Al, Mg, tungsten particles by combined MS/PECVD and the characterization of the obtained material;
3. Plasma transformation of powders and composites in order to change their surface properties, and if possible the particles size. Study of processes of particle destruction by laser and plasma means.

In a first approach, pulsed laser deposition (PLD) of a metal target (W and Al) immersed in a liquid (acetone and water, respectively) was used as a means to synthesize W and Al metal particles, as illustrated in Figure 1.

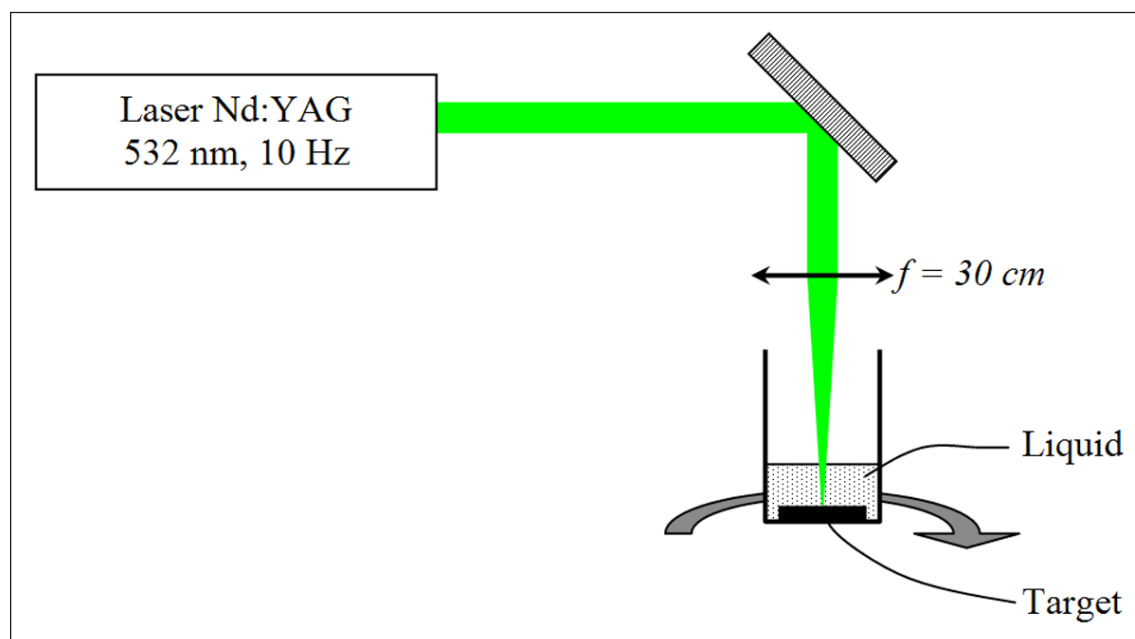


Figure 1. Schematic representation of the experimental setup.

The morphology of the laser processed particles was investigated by means of scanning electron microscopy. Energy-dispersive X-ray spectroscopy analysis was used to reveal the composition of resulting particles. The size-distribution histograms of the as-synthesized particles were inferred from the SEM micrographs using computer imaging software analysis.

SEM analysis of synthesized particles reveals that they are generally spherically shaped, with diameters usually of the order of several tens of nanometers, in some cases going up to hundreds of nanometers, as shown in Figure 2. Therefore, we can assert that for both targets (Al and W, respectively) and for both media considered (acetone and water, respectively) the synthesis of nanoparticles was achieved.

Significant differences between the nanoparticles states of aggregation on the substrate following evaporation have been observed. Nanoparticles processed in water maintain a better dispersion on the substrate surface, as compared to those obtained in acetone, allowing for the determination of their size distributions using computer imaging software. Particles size distributions peak are relatively narrow, peaking at 50 - 70 nm. There are, however, notable differences between the shapes of the distributions of Al particles sizes processed in water at a laser fluence of 20 J/cm² and that of W particles obtained in water at a laser fluence of 28 J/cm², a significant portion of these latter ones having sizes in excess of several hundreds of nanometers.

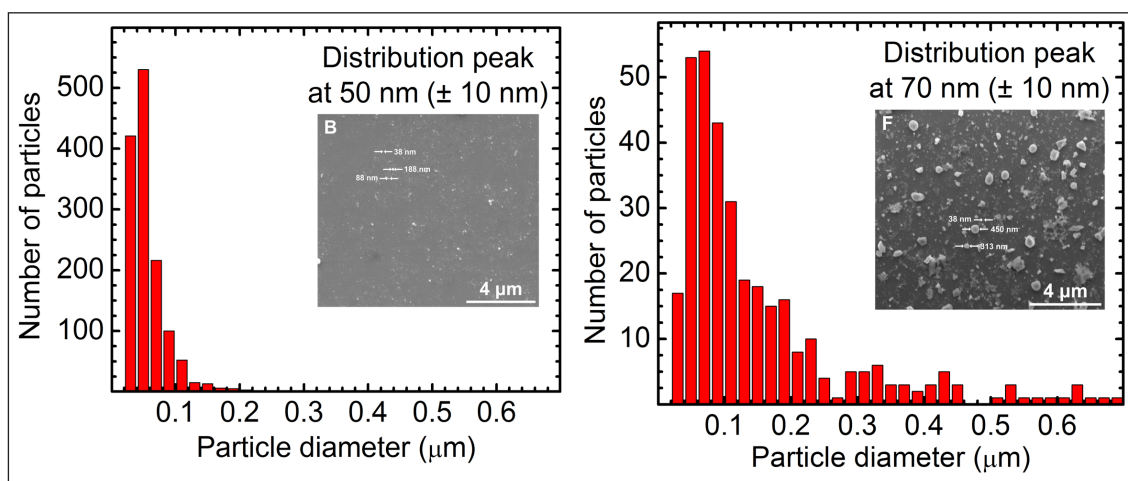


Figure 2. Computer imaging software generated histograms of particles sizes for samples B and F.

A pronounced agglomeration of Al and W particles, as well as strong C contamination, was observed for all samples processed in acetone. EDAX measurement confirmed the presence of Al in nanoparticles observable in the SEM images of samples A and B. Given these results, future experiments of treatments and environmental/toxicology studies of by-products expected to be created in next-generation nuclear fusion reactors could be initiated using such particles.

These first year results were disseminated in the form of a contribution at the 11th International Conference on Laser Ablation (November 13-19, 2011) in Cancun, Mexico, and a manuscript has been submitted for publication.



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The experiments performed at the Large Hadron Collider (LHC) in CERN are expected to reveal evidence of fundamental aspects theoretically predicted in high-energy physics such as the existence of the Higgs boson and the validity of the supersymmetry model. The huge amount of raw data acquired by the LHC detectors is forwarded to the LHC Computing Grid (LCG), which consists of a hierarchical structure of Tier0 (CERN), Tier1 and Tier2 computing centres distributed in the whole world.

High-energy collisions of protons and heavy-ions in the LHC produce an increasing flow of experimental data that are numerically processed and stored within the LCG. The experiments' output resulting from heavy ions collisions generates significantly larger amounts of data and longer processing times for single events. To preserve the rate of event transmission between the Tier1 and Tier2 Grid centres, which is essential for data analysis, the transmission throughput must increase accordingly. In these circumstances specific issues must be solved for ensuring the efficiency of data handling between the Tier1 centres and the associated Tier2 centres, and data analysis within the Tier2 centres.

HaPPSDaG focuses on the collaboration between IFIN-HH and IRFU-CEA/Saclay regarding the design and implementation of scalable solutions for improving the transfer, processing and storage of large datasets at the Tier2 centers that participate in the computing support of the ATLAS experiment within the framework of the LCG community known as the French Cloud. The project objectives are strongly related to the collaboration requirements concerning: a) the improvement of the communication and coordination between the Grille de Recherche d'Ile de France (GRIF) and the Romanian Grid sites; b) testing and improving the quality of the data link between the French Cloud and the Romanian centres for large dataset transfers; c) the implementation of specific technical measures for increasing the ATLAS job load and the storage performance in the Grid centres; d) the improvement of the data analysis in the Grid sites that are associated to the FR-Cloud; e) the participation of the Romanian staff in the grid monitoring and technical support within the ATLAS FR-Cloud; f) provision of training by the French staff regarding the Grid monitoring and support activities; g) dissemination of results.

During the first year of the project the work was focused on: a) an extensive analysis of the Tier1-Tier2 communication, in order to establish good interaction paths between the partners and to identify the weak points of the data connection between the grid centres; b) performance of studies and development of software tools for the monitoring and operation of the Grid connection between the French Cloud and the Romanian sites; c) investigation and improvement of the ATLAS job loading on sites, and of the data handling and processing within the French Cloud.

Important steps were made towards developing the Grid computing and monitoring

environment, especially for ATLAS data analysis. Performant software tools were implemented for the monitoring the data transfer and the storage performance of the Grid sites. These tools also provide the needed help in understanding the motives of lower performance of the sites which helped in finding appropriate means for improving the LAN throughput at IFIN-HH, its connectivity with the FR-Cloud, and the job loading on the workernodes. Scalable solutions were designed and implemented for improving the transfer, processing and storage of large datasets at the Grid centers that participate in the ATLAS data analysis.

A significant contribution to the performance management of the Romanian sites came from the implementation of an NGI-independent set of tools for monitoring the data transfer and storage efficiency in the resource centres. The improvement of the Grid productivity was measured through intensive data transfer and distributed analysis tests.

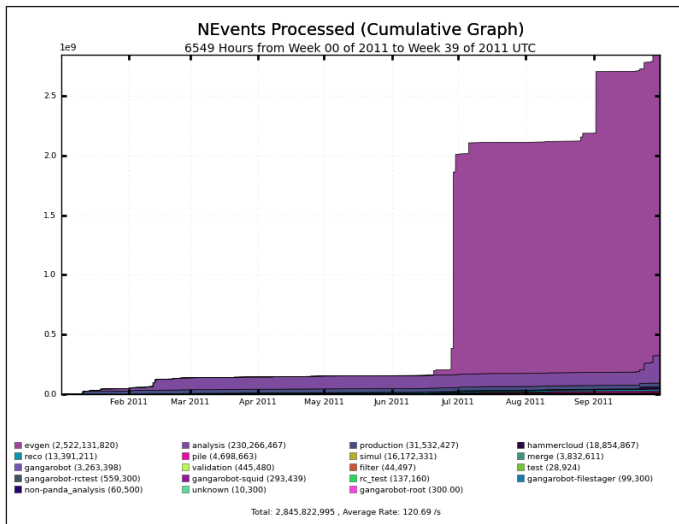


FIG.1: Integrated number of ATLAS events processed at the RO-07-NIPNE site between Jan. and Sept. 2011.

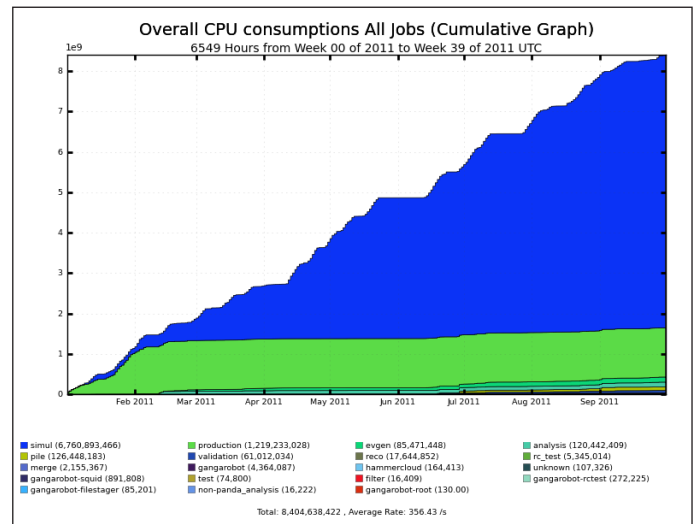


FIG.2: Cumulative graph of the overall consumption of CPU hours at RO-07-NIPNE between Jan.-Sept. 2011.

As a result, relevant Grid productivity parameters, such as the number of events processed and the cpu hours consumed by ATLAS jobs, have significantly improved (see Figures above).

A training stage was performed by a Romanian researcher at CEA/IRFU, in order to prepare the participation in the monitoring of the Grid centres and Grid jobs in ADCoS (ATLAS Distributed Computing Operations Shift) as well as to monitor the FR Cloud support team (Squad). Starting 2012, the Romanian team will participate in the ADC monitoring shifts and/or to the monitoring, at expert level, of 16 FR Cloud sites (in Tokyo, Beijing, Lyon, Marseille, Clermont-Ferrand, Grenoble, Paris, Orleans, and Romania).

The results, the status of the project at the end of its first year, and the specific action points to be further followed in order to implement the planned strategy were discussed by the French and Romanian teams at the 1st HaPPSDaG workshop entitled Large-scale Grid computing within the French Cloud, Bucharest, 2011.

The results obtained during the first year of the project will be published in the communication Grid and HPC support for national participation in large-scale collaborations, by M. Dulea, Ș. Constantinescu, M. Ciubăncan, et al., accepted at the 5th International Conference "Distributed Computing and Grid-technologies in Science and Education", JINR, Dubna, 2012.



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General objectives:

1. Elaboration of theories and conceptual models regarding the synthesis methods for the preparation of doped TiO₂ nanostructured compounds
2. Realization of an experimental model for the synthesis and characterization of C-doped TiO₂ nanoparticles
3. Realization of an experimental model for the synthesis and characterization of S-doped TiO₂ nanoparticles
4. Realization of an experimental model for the synthesis and characterization of TiO₂ nanoparticles with siloxane polymer coatings (optimization, selection, specific photovoltaic activity)

Objectives of Romanian Lab for 2011:

- (i) To synthesize pure and carbon coated TiO₂ powder at low cost in a single-step laser pyrolysis using TiCl₄ vapour as precursor with argon gas as a carrier, air as oxidizing agent and acetylene gas as a C precursor
- (ii) To characterize them with regard to phase(s), morphology, average particle size and surface area, carbon content

Results:

The laser synthesis aimed to carbon doping of TiO₂ nanoparticles.

On the basis of numerous adaptations/improvements of the experimental installation (2010) two main sets of experiments were performed, in which either acetylene or methyl methacrylat (in different concentrations) were used as carbon precursor.

- TiO₂ nanoparticles through the laser pyrolysis of TiCl₄ (vapors) were obtained. Alternatively the pressure in the reactor and the laser power were varied, in order to maximize the anatase phase of the nano-powders chemical content;
- C-doped TiO₂ nano-powders were successfully prepared;
- There is an optimum pressure for which high anatase percent and low-dimensions crystallites are found (Figure 1.a.);
- The increase of laser power leads to an increase of the rutile-TiO₂ phase;
- At the increase of the acetylene concentration, decreased crystallite dimensions (from about 21 nm to 18 nm) appear;
- Samples of TiO₂ and C-doped TiO₂ were sent to the French partner, in order to perform complementary characterization (such as Diffuse Reflectance measurements (Figure 1.b.), XPS and chemical test on the oxidative character of the obtained nanopowders).

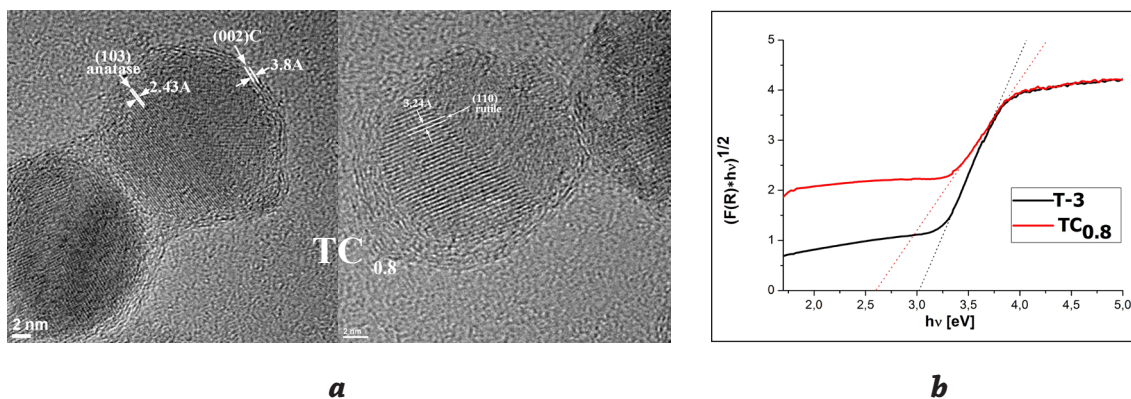


Figure 1. (a)-The interlayer distances marked on the images for sample TC 0.8; (b)- Absorbance spectra for the indirect electronic transition $F(R)^{1/2}$ vs E (eV) of the synthesized TiO₂ samples

Objectives of French Lab for 2011:

Synthesis and structural characterization of TiO₂ based nanoparticles synthesized by laser pyrolysis using titanium precursor (TTIP, titanium tetra isopropoxid) and the gaseous sensitizer.

Results:

- The study of TiO₂ nanoparticles through the laser pyrolysis in terms of influence of the parameters controlling the structural organization (the time of residence, the focusing of the laser, the presence of a sensitizer and the laser power);
- The effect of the crystalline phase on the position of the optical gap;
- N doped TiO₂ nanoparticles, prepared in one step method, using the addition of NH₃ in the reaction zone, present optical properties in the visible range;
- Synthesis and characterization of suboxide nanoparticles synthesized in high temperature condition, the longest residence time in the reaction zone seems to favor the Ti₄O₇ phase;
- Within the frame of a collaboration, the X-Lim laboratory (University of Limoges) developed a process in order to incorporate laser- synthesized TiO₂ nanoparticles in a solar cell and the efficiency of these first cells was found to be competitive with the state of the art.

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Ferroelectric and diluted magnetic semiconductor based multiferroic heterostructures for energy applications



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Ferroelectrics and multiferroics materials are potentially very important for a wide range of applications, due to the presence of the spontaneous polarization, high dielectric constant, non-linear optical properties, piezoelectric and pyroelectric effects, magnetoelectric coupling in multiferroics, etc. Diluted magnetic semiconductors (DMS) where ferromagnetism is established through indirect RKKY interaction, allowing electrical or optical control of the ferromagnetism have also a high technological potential. DMS oxides with room temperature ferrimagnetism are natural candidates to be interfaced with ferroelectrics, as recently demonstrated. MULTIFERRODMS will be the first project to combine both materials by synthesizing multiferroic heterostructures engineered from ferroelectric and DMS layers. The main goal is to provide a route to robust electrical polarization from rather weak magnetic polarization, triggered by light absorption. Thus, sufficiently high voltages may be provided by such devices to induce electrolysis in an integrated thin film light absorber - hydrogen generator. In the first stage of this project we will carry out a systematic investigation of a prototype ferroelectric, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), epitaxially grown as a thin film on a variety of substrates, creating a variety of different strain states. PZT has a high polarization ($120 \mu\text{C}/\text{cm}^2$), which can be adjusted by varying the stoichiometry. The Curie temperature may also be tuned by the in-plane strain. Due to the use of suitable substrates chosen for example from amongst SrRuO_3 (SRO), $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSMO), SrTiO_3 (STO), BaTiO_3 (BTO) and DyScO_3 (DCS), a wide range of compressive and tensile strain states will be available. These studies will investigate the quality of the epitaxial layers (in-situ techniques used: low-energy and reflection high energy electron diffraction: LEED, RHEED; X-ray photoelectron spectroscopy XPS, see Fig. 1) and about their properties, assessed by hysteretic cycles at different temperatures and stresses. The second idea of this Project is to work on artificial multiferroics which can be obtained by combining ferroelectric materials with diluted magnetic semiconductors (DMS). We estimate that a DMS system containing 1 % magnetic ions with $1 \mu_B/\text{atom}$ may generate a field of ~ 100 Oe at the interface. For a conversion factor of $1 \text{ V}/(\text{cm} \times \text{Oe})$ and a 1 mm ferroelectric film, a 10 V potential difference may be generated. The use of an oxide semiconductor for DMS, for example ZnO or TiO_2 will avoid many of the problems occurring at the interface with a ferroelectric or multiferroic oxide such as parasitic oxide phases, interdiffusion, accumulation of oxygen vacancies.

During the first year of the Project duration, three defined results were obtained:

(i) Synthesis and characterization of ferromagnetic FeSi phases on Si(001) [1]. This study presents a correlated study of structural, reactivity, and magnetic properties of ultrathin Fe layers grown on Si(001) by molecular beam epitaxy in ultrahigh vacuum. The interface reactivity is characterized by Auger electron spectroscopy. The surface structure is characterized by low electron energy diffraction with spot profile analysis. The magnetism of

the synthesized layers is investigated by magneto-optical Kerr effect. At room temperature, metal Fe layers with poor long-range order are synthesized; these layers are ferromagnetic with an extremely low coercive field (below 1 Oe). The reactivity with Si is low in this case, with formation of an interface layer of about 8 Å Fe equivalent thickness with about 7 at.% Si diffused. Samples synthesized at higher temperatures (500 °C) exhibit better long-range order, though the Fe reactivity with Si is higher and leads to the formation of an interface compound whose approximate stoichiometry is very close to Fe₃Si. Once this compound is formed, disordered metal Fe islands are developing with subsequent Fe deposition, which contain also about 8 at.% Si diffused. These structures exhibit a much lower ferrimagnetism, with saturation magnetization about one order of magnitude lower than in the case of the room temperature synthesis. In this case of high temperature synthesis, two phases are observed, a ferrimagnetic one and a superparamagnetic one.

(ii) Synthesis and characterization of thin PZT layers by PLD [2]. High quality pulsed laser deposited lead zirconate titanate (PZT) films are obtained by pulsed laser deposition on SrRuO₃(111) single crystal layers and characterized by X-ray photoelectron spectroscopy (XPS), to determine the surface composition. It is found that a minor amount of Pb forms PbO₂ at the surface and also some Pb is included into the contamination layer, in form of a Pb(CO₃)₂ layer of about 1 nm thickness, occupying about one quarter of the PZT surface. The stoichiometry of the outermost 4–5 nm layers yielded as PbZr_{0.25}Ti_{0.80}O_{2.5}, which suggest the formation of an oxygen depleted, Brownmillerite-like layer at the surface, of at least 5 nm thickness.

(iii) Studies by high resolution synchrotron radiation photoelectron spectroscopy and by photoelectron diffraction of ferroelectric surface structure of BaTiO₃ [3]. This work was performed in common during two stages at the synchrotron radiation facility Soleil, Saclay, France. The surface of a ferroelectric BaTiO₃(001) single-crystal was studied using synchrotron radiation induced X-ray photoelectron diffraction (XPD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and low energy electron diffraction (LEED). AFM, XPS and LEED show that the surface is BaO terminated with a (1x1) reconstruction. The Ba 4d, Ti 2p and O 1s XPD results were compared with multiple scattering simulations for out-of- and in-plane polarizations using a genetic algorithm to determine atomic rumpling and interlayer relaxation. Linear combinations of the XPD simulations of the surface structure of each polarization states allows determination of the domain ordering. The best agreement with experiment is found for 70% out of plane domain polarizations. The upward pointing polarization, P⁺, is dominant.

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The main objective of the project is to study the construction of the metal-ferroelectric interface and the dynamic of charge compensation in relation to polarization switching. The results will be compared to those of the macroscopic electric measurements performed on standard metal-ferroelectric-metal (MFM) capacitors. Also, the metal-ferroelectric interface will be compared with the results reported for the free surface.

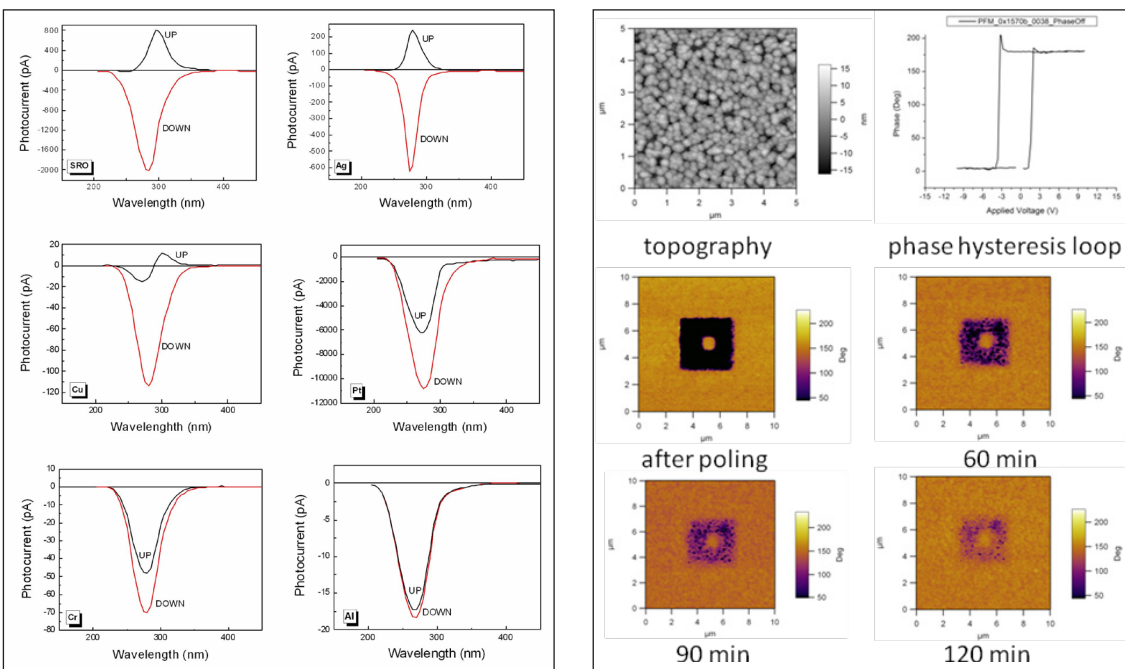
The entire project is based on the idea that, in a ferroelectric material with structural quality close to perfection, the polarization ends up with two sheets of surface charges, one negative and the other one positive. In order to have a stable polarization state, these charges should be compensated with charges of opposite sign, otherwise they will generate a depolarization field leading to formation of opposite polarization domains. This fact could have an impact on the formation of the metal-ferroelectric interface.

During the year 2011 several important results were obtained. These will be summarized below:

- The effect of the electrode interface on the photovoltaic properties of an epitaxial PZT thin film was studied by measuring the short-circuit photocurrent. The ferroelectric capacitors were obtained through the deposition of different metals as top electrodes on the same epitaxial layer of PZT grown by pulse laser deposition on single crystal $\text{SrRuO}_3/\text{SrTiO}_3$ substrate with (001) orientation. The SrRuO_3 layer of about 20 nm thick plays the role of the bottom electrode while SrRuO_3 , Cu, Ag, Au, Pt, Pd, Ni, Cr, Al were used as top electrodes. It was found that the magnitude of the short-circuit photocurrent and the shape of its spectral distribution are dependent on the metal used as top contact. Also, the internal bias influencing the change of the photocurrent’s sign when the ferroelectric polarization is changing its orientation is dependent on the metal used as top contact. All these results suggest that the photovoltaic properties of the epitaxial PZT films with thickness in the range of 50-250 nm are strongly influenced by the electrode interface. The highest value of the photocurrent was obtained for top Pt, suggesting that the combination Pt/PZT/ SrRuO_3 can be used for ultraviolet detection in the 200-400 nm wavelength range. For top SrRuO_3 and Ag the photocurrent is changing the sign when the polarization is changing the orientation, suggesting that the internal imprint is minimum in these cases. This behaviour can be useful for a non-destructive readout of the non-volatile ferroelectric memories providing that the written information is stable in time. The Al/PZT/ SrRuO_3 has a diode like behaviour. The results of this study were published in a paper with title “Interface controlled photovoltaic effect in epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films with tetragonal structure” (published in **Journal of Applied Physics 110, 044105, 2011**).
- A detailed investigation of the surface was performed by using combined XPS and AFM/PFM techniques. The XPS results have revealed that the bare surface of the epitaxial PZT

film is depleted in oxygen and has a very thin layer of about 1 nm thickness composed of parasitic phases, mainly carbonates. The investigations were performed on 300 nm thick PZT films. The AFM/PFM investigations have revealed the presence of ferroelectric domains (both a and c domains, however, with a dominance of the a domains, meaning that the ferroelectric polarization is mainly oriented parallel with the surface). The oxygen depletion of the surface was observed also in epitaxial BaTiO₃ films, suggesting that it is a common phenomenon for ferroelectric perovskites. The orientation of the ferroelectric polarization, as determined with PFM, is dependent on the film thickness. It was found that for thinner films the polarization is mainly oriented out-of-plane, with only few a domains present. The stability of the polarization seems to be dependent on the film quality, being enhanced in the epitaxial films grown by pulse laser deposition compared to those prepared by sol-gel (the last ones were samples provided by the French partner). Part of the above results were published in the paper with title “X-ray photoelectron spectroscopy of pulsed laser deposited Pb(Zr,Ti)O_{3-δ}” (published in **Physica Status Solidi A**, DOI 10.1002/pssa.201127740, 2012).

During the year 2011 several samples were prepared by collaboration between the Romanian and the French partners. All the samples were analyzed with X-ray diffraction, AFM/PFM and now are subject to electrical measurements after the deposition of top Pt electrodes. The samples prepared by the French partner, using the sol-gel method, on Si wafers with SrTiO₃ buffer layer deposited in France and bottom SrRuO₃ electrode deposited by pulse laser method in Romania, proved to be of high quality, comparable with that of the fully epitaxial structures grown on single crystal SrTiO₃ substrates. A common abstract was submitted for the **European Conference on Crystal Growth**, to be held in Glasgow, 17 – 20 of June 2012.



Left – spectral distributions of the short-circuit photocurrent recorded for different metals used as top electrodes, and for different orientations of the ferroelectric polarizations. Measurements performed on epitaxial PZT film with common bottom SrRuO₃ electrode. Right – time stability of the ferroelectric polarization in the case of a PZT film, deposited by the French partner on a SrRuO₃/SrTiO₃/Si substrate using the sol-gel method.

**Development of innovative binders for the stabilization/
solidification of low- or intermediate-level radioactive wastes
containing aluminium**



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Objectives

The project aims at investigating alternative cement systems to provide innovative solutions for the solidification and stabilization of problematic historic wastes containing aluminium metal. The objectives are threefold: (i) to compare the potential of calcium sulphoaluminate, magnesium phosphate, calcium phosphate and magnesium silicate binders to mitigate the release of hydrogen by a solidified waste form due to corrosion of aluminium, (ii) to assess the feasibility to reduce the corrosion of aluminium still further by the addition of a corrosion inhibitor in the mixing solution, and (iii) to develop, for the two most promising cementitious systems selected from steps (i) and (ii) a formulation checking the desired criteria for waste conditioning. The project will involve multi-disciplinary research groups with skills in materials science, physico-chemistry, analytical chemistry, and process engineering.

Step 1: Screening of binders (2012)

Pastes will be prepared with cements from the four investigated systems (calcium sulfoaluminate, magnesium phosphate, calcium phosphate, and magnesium silicate), with or without aluminium. The phase assemblage of the hardened materials will be characterized using X-ray diffraction and thermogravimetry. The pore solution of the material will be extracted using pressure and analysed by ICP-AES, pH-metry and ionic chromatography.

The production rate of hydrogen by samples containing aluminium will be investigated, periodically sampled and analysed for its hydrogen content using gas chromatography. At the end of the trials, the transition zone between metal and cement paste will be characterized using scanning electron microscopy, EDS analysis, and X-ray diffraction; the different cementitious systems will be ranked as a function of their capability to mitigate aluminium corrosion.

Step 2: Investigation of corrosion inhibitors (2013)

The corrosion rate of aluminium will be measured as a function of the nature and concentration of the inhibitor added to the synthetic pore solution of the most promising binders identified in step 1, binders as well will be investigated. The influence of the inhibitor on the properties of the hardened material (strength, volume stability) will also be assessed. Finally, aluminium rods will be encapsulated using the most promising cements and inhibitors, and the materials will be characterized as previously described in step 1 (hydrogen production rate, solid phase assemblage, microstructure and composition of the transition zone between the binder and the aluminium rod).

Step 3: Design of a cement formulation checking the criteria for industrial application and final disposal (2014)

The third step of the project will aim at designing a pumpable, flowable and self-levelling grout using the most promising binders and inhibitors. The material will also have to check the specifications for a final disposal of the waste packages in a surface repository. The investigated recipes will be tested at the laboratory scale and optimized for their cement, water, and sand contents. The elaborated materials will be characterized using the conventional tools of civil engineering. Particular attention will be paid to the heat output at early age, in order to keep an acceptable thermal excursion when the grout will be cast in large volume canisters. Experimental matrices will be prepared and disposed in simulated (fast damaging) and normal repository (Romanian National Repository for Radioactive Waste Baita-Bihor) conditions.

Step 4: Experimental data correlation in order to validate the optimum matrix for conditioning low-or intermediate-level radioactive waste containing aluminium (2015)

In the last step there will be made a detailed evaluation of the results obtained in order to choose and validate the optimum recipe for preparing the innovative materials for conditioning low-or intermediate-level radioactive waste containing aluminium. Also the aspects that require further investigation will be pointed out, sketching new possible ways to approach them and opportunities for future collaboration.

Anticipated outcomes

The project will help finding a solution to treat problematic wastes containing aluminium. It will also improve the knowledge of alternative cement systems, and their interaction with electropositive metals. It should be recalled that, up to now, these wastes cannot be encapsulated in a cement matrix and are temporarily stored in silos and ponds. From a scientific point of view, the project will provide a better understanding of inorganic binders which are much less known than ordinary Portland cement.

Cooperation perspectives

It would also be a way to continue, in a bilateral form, the more informal cooperation initiated within the framework of the IAEA Coordinated Research Project on cementitious materials for radioactive waste management (2007-2010) in which both the CEA/L2ED (France) and the IFA (Romania) were involved.

In the future, the initiated cooperation between CEA and IFA concerning aluminium-containing wastes might be extended to the conditioning of other types of wastes.

Functional surfaces obtained by electroplating of nano-sized dispersed ceramic phases with metals for use in the nuclear industry to increase the corrosion and tribocorrosion resistance



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Project motivation

Conventional metals and alloys perform poorly in many applications where metal components are subjected to aggressive environments and erosive conditions. Corrosion and wear resistant coatings are frequently needed in applications such as mechanical parts under friction, micro devices and nano devices; steel conveyors exposed to ambient air of high relative humidity, electrical connectors in the automotive industry, hip prosthesis, and turbine blades. The project aims at fabricating nano structured metal matrix composite coatings using electrodeposition and co-deposition techniques of nanosized ceramic phases with metals (Co, Ni, Zn, Cu).

Significantly improved tribological and corrosion properties are desired from these nanostructured coatings. A parametric study will be performed to obtain nano composite dispersed coatings with minimum defects, excellent adhesion, enhanced corrosion resistance and mechanical properties. These will be then characterized in terms of their complex properties for new fields of use. Degradation phenomena occurring in processed materials such as corrosion, wear and tribocorrosion will be studied in detail. Aqueous corrosion will be studied using electrochemical techniques. Sliding wear will be studied using pin-on-disc configuration. Tribocorrosion tests will be performed to simulate corrosion-wear behavior of the processed nanocomposite coatings. Underlying damage mechanisms will be investigated.

Project objectives:

- Making functional nano-structured surfaces by electrolytic deposition of nano-dispersed particles (mechanism and kinetic of co-deposition process of nanodispersed phases with metals);
- Investigation of the mechanism of functional surfaces repassivation kinetic by in situ electrochemical investigations (free potential during intermittent friction potential-dynamic curves with and without friction, impedance diagrams of surfaces in passive and active state, potential jumps from active to passive recording the current by monitoring the development and growth of the passive film);
- The corrosion and tribocorrosion tests on functional surfaces as nano-structured composite coatings;
- Elaboration of the repassivation mathematical model depending on time and layer thickness based on in situ and ex situ electrochemical measurements, the surface structure and composition.

These studies will enable to understand both the damage mechanism in such coatings and the co-deposition phenomena.

Expected results and foreseen advantages:

This research project is expected to result in joint publications in refereed journal and conference proceedings. Further long term research ties will be established with each other, especially in the area of synthesis of materials using electrodeposition techniques.

The collaboration with the French institutions will enable the pool of different complementary knowledge on the complex phenomena of nano structured composite functional layers and corrosion – tribocorrosion characterisation. The LGPM / ECP laboratory has a deep experience of the fundamental nature of the mechanisms and corrosion/tribocorrosion processes analyzed through in-situ and ex-situ methods whereas the CEA/LISL laboratory has skills in surface characterization. On the other hand, the rich experience of the CC-ITES / UDJG partner in composite coatings by electrochemical methods shall be enriched with the complete characterisation of the above-mentioned functional surfaces which shall further facilitate the identification of the most widely used scopes of applications.

The techniques available in the three laboratories together with the competence of the research groups/teams are complementary and cover the broad field of testing procedures and data necessary for the advanced tribocorrosion studies on nano and structured composite functional layers (mechanics, tribology, metallurgy, electrochemistry, surface analysis, ultrahigh microtopography, etc.).

The project must allow the partners to put together their expertise and know-how in a prospective survey of the preparation and the behavior of nano structured composite materials for nuclear industry. The project will also allow them to pursue the development of a high-level scientific collaboration between CEA Saclay - France, Ecole Centrale Paris - France and Competences Center Interfaces –Tribocorrosion and Electrochemical Systems (CC-ITES) from Dunarea de Jos University of Galati (UDJG) - Romania.

Cooperation perspectives:

- Obtaining and complex characterization of nanocomposite coatings by electrochemical processes, with potential innovation impact in the field of nanomaterials and nuclear industry applications.
- Creating the polls of excellence in the field of nanostructured functional surfaces obtained by electro-co-deposition of nanosized ceramic dispersed phases with metals, corrosion – tribocorrosion by UDJG-CC-ITES (RO) and CEA Saclay –Ecole Centrale Paris (F).
- International visibility of research teams from both countries, through publications, international conferences and others project proposals.
- Training of Human Resources to improve the quality of the research through by enhancing the mobility of young researchers and PhD students.

AMS analyses of concentrations of hydrogen isotopes and other elements in tiles dismantled from the Toroidal Pump Limiter at Tore Supra Tokamak



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Since the last nuclear incident in Japan the need of a much more secure nuclear energy reactor based on fusion became an imperative task of our days. Tore Supra is an outstanding Tokamak working on this goal and as many other large fusion faculties in the world is employing over 100 diagnose tools to accomplish this task. Out of these, the Accelerator Mass Spectrometry (AMS) has significantly risen to the level of supremacy of its kind contributing to a more sensitive diagnose and analyses of particle transport studies, erosion deposition studies, characterisation of plasma facing components and dust, plasma confinement and detachment, divertor load, etc. AMS is a powerful and modern analysing method that was applied at JET and ASDEX-Upgrade but, unfortunately, not yet applied at Tore Supra [1, 2].

AMS, totally opposite but complementary to the classical techniques, is not detecting the radioactive agents by their emitted radiation (α , β , γ), but it selects and counts them individually, one by one, each radioactive atom. The AMS method has the highest analyzing sensitivity known today, which is 10^{-15} (ratio: isotope/element). This sensitivity is equivalent with the real possibility to select and register one single type of atom from a million of billions of other types of atoms. The AMS facility is complex, gathering many modern methods from accelerator, atomic and nuclear physics like accelerator and focusing elements, electromagnetic analyzers, and particle detection systems etc. Fig.1 shows the main components of the experimental set-up from NIPNE, Bucharest [3].

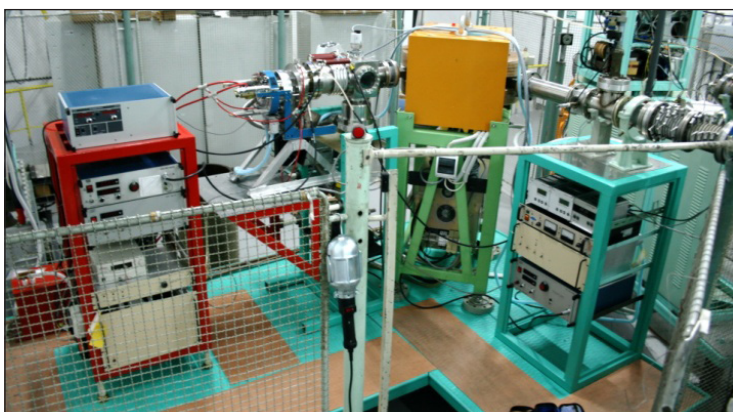


Fig.1 Left: AMS injector, Right: 9MV tandem accelerator from NIPNE.

The main objective of this project is to study the particle accumulation in the Toroidal Pump Limiter at Tore Supra.

Since this assembly is removing the most of the emitted particles during the fusion discharges the AMS analysis of concentration depth profiling of different elements would provide interesting information not only about particle transport and erosion deposition but will reveal also information about the fusion efficiency during the tokamak discharges.

We will analyze by AMS samples cut from tiles dismounted from the toroidal pump limiter, located in the center of the limiter. These samples were exposed to the plasma discharges in the Tore Supra and AMS will determine the deuterium concentration depth profile and the deposition of other elements on the surface. The poloidal distribution of particle retention on the limiter will also be studied. The samples will be cut from locations on tiles situated in radial direction.

Further on, dust from Tore Supra and JET will be measured. The collection of dust will be performed in relevant locations. The only problem of analysing dust by AMS is the possibility to press the dust in solid form. A rather complete elemental analysis of dust can be achieved.

Another important part of the project will be dedicated to the elemental deposition studies on the protection tiles. By using AMS and other conventional methods the element deposition on tiles from the toroidal pump limiter at Tore Supra will be determined.

In the future, this project, performed within the frame of CEA - IFA (NIPNE) cooperation, will open new perspectives for other joint researches. These could have even more important tasks to solve for the international project ITER. It is most probably that the cooperation between the two partners will be consolidated and it is probable to apply for a FP8 project.

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Creation of national standards for some emerging pharmaceutical radionuclides to ensure the radioprotection of patients and medical staffs



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The objectives of the research project are:

1. Approach of the radionuclides of mutual interest, used for targeted therapy or diagnosis: ^{186}Re , ^{82}Sr - ^{82}Rb , ^{177}Lu , ^{90}Y .
2. Common measurements to obtain primary standards of these radionuclides, by using absolute standardization methods: the LSC-TDCR liquid-scintillation counting, the $4\pi\beta$ - γ coincidence and the calorimetry technique.
3. Delivery of an ampoule containing the same nuclide to the BIPM for participation to the international System of References (SIR) in order to create or improve the international Key Comparison Reference Value (KCRV).
4. Theoretical and experimental studies to improve or determine the nuclear decay scheme data of these nuclides, important for the dose calculations. A new decay scheme will be established in the framework of the international co-operation "Decay Data Evaluation Project" (DDEP). The NUCLEIDE database (http://www.nucleide.org/DDEP_WG/DDEPdata.htm) will be updated.
5. Creation of secondary standards through the Ionization Chambers (IC) or gamma spectrometry (GS) instruments which can be easily transferred to the nuclear medicine services in hospitals.
6. Dissemination of the results obtained, by common participation in international conferences / workshops and publishing articles in international ISI-quoted journals.

The working plan has the following steps:

1. Purchase, assembling, testing and calibrating of a new X-ray spectrometric system at IFIN-HH
2. Study of the radionuclides ^{186}Re and ^{177}Lu : purchase of radioactive solutions, documentation, common activity measurements and comparisons, nuclear data measurements and evaluation, reporting and writing articles for journal publishing.
3. Common measurements of ^{82}Sr - ^{82}Rb and ^{90}Y at CEA/DRT/LIST, LNHB. Organization of an international workshop by IFIN-HH.
4. Writing a common paper for publication. The final report of the project.

The most important estimated results of the project are:

- the elaboration of several scientific papers presented in international conferences and published in ISI-quoted scientific journals.
- the implementation of the national and international activity traceability chains for the studied radionuclides.
- new nuclear decay data evaluations for three radionuclides, participation to the international databases.

Regarding the foreseen impact of the project, there are several aspects to be mentioned:

- Scientific impact: papers to be published and presented in international conferences, new nuclear data for international databases;
- Technological impact: establishment of the metrological activity traceability chains for new radionuclides of medical use.
- Educational impact: training of two young Romanian researchers at CEA/DRT/LIST/LNHB.
- For both laboratories, the economic impact results in the possibility to calibrate the activity measurement installations (radionuclide calibrators) from the hospitals in both countries; support and metrological traceability to some radiopharmaceuticals producers will be provided.
- The social impact will consist in improving the efficiency of the radioprotection methods in hospitals, by allowing precise measurements and accurate evaluation of the irradiation doses for patients and medical personnel.

The completion of the project will reinforce the collaboration between IFIN-HH and CEA/DRT/LIST/LNHB, both bilateral and international (such as European Metrology Research Programme – EURAMET EMRP A169).



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The project objective is to highlight the major contributions that could be made by engineered particles of hydroxyapatite and complex ceramic matrices for environmental applications such as soil and groundwater remediation. The project will test methods to obtain porous materials able to retain inorganic and organic pollutants in the laboratory that will be implemented in real contaminated sites.

The purpose is to develop scientific research on phosphocalcic apatite in order to exploit those phosphates that represent a form of natural wealth and to prepare a porous material, capable of effectively eliminating inorganic pollutants like heavy metals from contaminated soils and water.

The main goal of this project is to put in place a new method of synthesis and elaborate solid apatitic matrices capable of retaining inorganic pollutants. Our studies will be focused on Pb^{2+} ions. The study of Pb^{2+} ions adsorption on the porous apatite and commercial apatite in the aqueous medium will be conducted. The comparison between the adsorption properties of Pb^{2+} ions on the commercial apatites and the synthesized apatites represent another target of this project and also a novelty in the field.

The apatites have tunnels and some active areas responsible for the adsorption phenomenon. The research involving the adsorption properties of porous and poorly crystallized apatites are rare. The lack of accurate studies in this area has led us to study the properties of heavy metal ions adsorption on porous and commercial apatite aqueous medium. A study of the adsorption isotherms will also be conducted. We will perform as well a comparative study between the properties of trace metals adsorption by commercial porous apatite and by synthesized apatite.

First, the development and characterisation of phosphocalcic apatite and surface modification of calcium phosphate apatites in aqueous medium and characterization will be conducted. Porous hydroxyapatite will be prepared in aqueous medium at different reaction temperatures.

Second, structural and morphological characterization at the nanoscale of the nanoparticles will be performed. The obtained materials will be characterized by adequate physico-chemical techniques such as: X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), infrared spectroscopy (FT-IR), thermal analysis (ATG and ATD), chemical and elemental analysis, determination of specific surface area (BET method), porosity studies using ultrasounds, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, photoluminescence, UV-Visible spectroscopy, electric properties. Additional porosity studies using ultrasounds will be carried out. It will include complex studies based on multiple scattering of ultrasound waves. Characterization of equivalent density and porosity can be done using a numerical model based on finite element method.

Model parameters will be correlated with experimental data. These data will be obtained as a result of determinations made in specialized laboratories in the country and abroad. The apatite pills obtained with different preparation parameters can thus be characterized in a non-destructive and non-invasive way, using ultrasounds. The method is based on the reflexion/transmission of ultrasonic waves through the air.

Third, the characterization of physico-chemical properties and surface reactivity of nanoparticles in solution, in terms of colloidal stability and affinity to organic and inorganic pollutants, will be conducted. The reactivity of particles of nanometric sizes strongly differ from the same materials of micro or millimeter size, suggesting that the adsorption mechanisms differ depending on the size. To understand the reasons for such a difference, the surface reactivity of the nanoparticles will be studied in terms of differentiation of surface sites and adsorption capacity of pollutants. Evaluation of efficiency retention of Pb^{2+} and other metal compounds on porous hydroxyapatite will be conducted. Correlation between structural and adsorption properties of porous hydroxyapatite will also be studied.

The project will conclude with the definition of laboratory technology for (i) synthesis of porous hydroxyapatite for immobilization and / or separation of organic and inorganic pollutants, (ii) synthesis of apatite matrices able to immobilize and / or separation of inorganic and organic pollutants (iii) models for calculating the equivalent density and porosity based on finite element method.

Producing phosphocalcic apatite in order to exploit phosphates which are widely spread in natural environment and preparing a porous material able to immobilize and / or separate the organic and inorganic pollutants represents a major contribution of this project. On the other hand, the development of a new method of synthesis could lead to obtaining depolluted low cost materials that might be possible to be widely implemented.

Contaminated soils present a huge environmental problem in developed countries that have many abandoned post-industrial sites. Contamination of soils and groundwater by inorganic (nitrates, trace metals and metalloids) and organic pollutants (pesticides, herbicides, PAHs etc.) is indeed an international problem. The project objectives are to highlight and demonstrate the major contributions that could be made by engineered particles of hydroxyapatites, and apatite matrices for the removal or immobilisation of inorganic (metals, metalloids, nitrates) and organic pollutants (herbicides, PAHs). Our project provides the first intercomparative integrated research on synthesized mineral particles for the removal or immobilisation of inorganic and organic pollutants.

The results can form the basis of greater cooperation in international programs such as FP7 and FP8 but also under contracts that concern remediation of industrial wastewater and / or soil. During the project other topics of common interest can also appear in national and international programs, to be submitted in the next five years.

Incorporated surface plasmons into core-shell fluorescent nanoparticles using microemulsion assisted photoreduction technique



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Plasmonics has been recognized as the technique, which enables the strongest electromagnetic field confinement. Now, advanced research is concentrated on enhancement of the interaction of the passive plasmonics, with active media, capable of generating, enhancing, transforming or converting optical field, research which evolved from Surface-Enhanced Raman-spectroscopy (SERS) to plasmon-mode lasing. Nanoparticles (NPs) and other finite-sized nanoscopic noble metal system exhibit many unique properties, different from their bulk counterparts, arising from the existence of confined plasmon modes localized on its surface.

A drawback is represented by the poor control of the optical losses induced by the metal surface, which is the most important factor generating the Forster energy transfer. Another important difficulty preventing systematic studies of the interaction between plasmons and dyes is the lack of control over the dye-particle geometry. And on the molecular-scale structure of the hybrid objects, the positioning of the chromophore molecules or aggregates relative to the metal surface being poorly known random parameters.

The objective of this project is to develop incorporated surface plasmons into core-shell fluorescent NPs using microemulsion assisted photoreduction technique, approaching two routes:


- a) hollow NPs encapsulating chromophores: chromophores are encapsulated in hollow Au NPs to form J aggregates;
- b) NPs coated with a silica layer to which chromophores are covalently bonded: Au NPs represent the core and the core-shell is represented by chromophores bonded to silica.

The main specific scientific objectives which are addressed during this project are:

1. Design, synthesis and stabilization of Au NPs coupled with J-aggregated dyes that allow enhancement of fluorescence intensity
2. Optimization of synthesis of 'bulk' and hollow Au NPs coupled and combined with J-aggregates
3. Evaluation of optical properties of Au NPs coupled with J-aggregates

So, the core challenge of the present project is to obtain noble NPs (Au) combined with chromophores molecules that exhibit fluorescence enhancement by using the microemulsion assisted photoreduction technique, which allows for high flexibility in synthesis and materials selection. In general, the approach has several beneficial aspects:

- i) the microemulsion approach can be widely modified by adjusting the type and amount of polar/nonpolar phase and surfactants, this allows for fine-tuning the micelle diameter by controlling the diameter of the resulting NPs.

- 
- ii) the possibility to establish water-in-oil-(W/O)-as well as oil-in-water-(O/W) microemulsions - increases the experimental flexibility of the approach.
 - iii) the reduction reaction on metallic precursor is conducted under UV light, and this reduces chemicals consume and thus their side effects.
 - iv) a wide type of metallic NPs is accessible, ranging from those with positive reduction potential to the ones with negative, or from typical 'bulk' to hollow NPs.
 - v) while establishing the sphere wall of the hollow spheres, all compounds dissolved inside the micelle are encapsulated,so that microemulsions gives direct access to container-type functionalities.
 - vi) the location of the chromophores molecules or aggregates can be directed and also the reason for their preference among oil-in-water interface, can be elucidated based on their spectral behaviour.

Forseen impact: The final goal of the project is to demonstrate the possibility of using microemulsion assisted photoreduction technique for controlling both the energy and electron transfer processes between the chromophore molecules and the gold nanoparticle with the enhancement of the fluorescence intensity. The demonstration of such bottom-up assembly processes by adapting soft nanotechnology techniques would open interesting perspectives in the whole domain of nanosciences and nanotechnology from biology (drug nanovectors) to optoelectronic devices. Indeed, these results would offer a complete predictive control over the plasmons surface. This comprises both the relative positioning of the fluorophores and their interaction with metallic nanoparticles associated with the characterization of luminescence properties, including its dynamics, is expected to provide a deep understanding of the rich photo-physics of such systems.

Interest and perspectives of collaboration: Most common research activities deployed on self-assembled nanoporous molecular networks, the obtention of organic or inorganic nanoparticles, the conduct of different reactions inside of nanodroplets, the incorporation of nanoparticles inside nanoporous monolayers provide the basis for developing a successful collaboration between the partner institutions, CEA Saclay and University POLITEHNICA of Bucharest.



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The goal of this project is to develop novel techniques for assessing biosensor surfaces built with self-assembled monolayers (SAMs) as well as the design of the biosensor and its testing. The main tasks of this project will be: (i) to perform reproducible characterization of a biofunctionalized surface in order to analyze the distribution of single proteins and evaluate their capacity of binding metals of interest. Main characterization techniques involved will be scanning probe microscopy in imaging and spectroscopic modes giving information on the surface coverage and mechanical properties of the layer, its surface contact potential and dielectric constant variations, as well as confocal RAMAN microscopy for complementary characterization. (ii) to design the biosensor and to perform its testing, mainly involving Electrochemical Impedance Spectroscopy (EIS) and related techniques.

Methodology and work plan

WP.1. Developing self-assembled monolayers (SAM) on silicium and gold

Collaborators of the LIRM (B. Bennetau) possess all the required skills for preparation of functional self-assembled monolayers (SAMs).

Task 1.1. Identifying monoclonal antibodies/receptors that will bind to the heavy metals

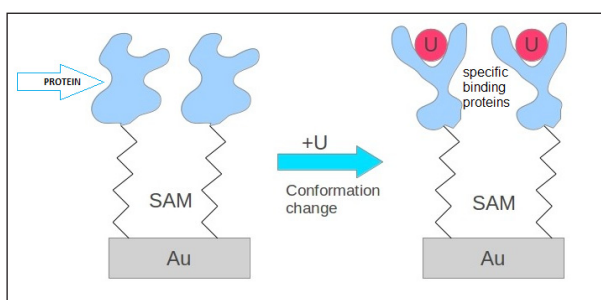
Identifying a surface with a high specificity would ensure the discrimination needed for detecting only heavy metal ions as opposed to other ions present in solution.

Task 1.2. Including the Identified antibodies/receptors on SAM on silicium and gold

The monoclonal antibodies or receptors identified in the previous task must be immobilized on a substrate.

WP.2. Characterization of self-assembled monolayers before/after bonding with heavy metals

We will focus on characterizing the SAM covered substrates in order to ensure a good distribution of the proteins and to avoid steric hinderance. After the heavy metal ions have bonded with the protein we expect to see differences in the mechanical and electrical properties of the sample.



Task 2.1. Micro Raman characterization

The first characterization of the samples will be done using a Raman-Confocal microscope. This method provides “fingerprint” spectra that are unique to each specific compound and contain information about chemical composition and structure.

Task 2.2. AFM and SPFM studies, heavy metals (HM) interactions and electrical properties mapping

Surfaces will be characterized by AFM with the novel peak-force scan Assyst™ mode which allows to image biological molecules with lower forces. The surfaces will also be characterized by SPFM offering the possibility of mapping several properties such as surface contact potential, local charges, dielectric constants, etc.

WP.3. Bioeensor design activities: Characterization of electrochemical behavior of SAM in a solution of heavy metals

The other major goal of the project is to develop a biosensor based on selective SAMs and a gold reference electrode. Its characterization and testing is also one of the main purposes of this work package.

Task 3.1. Cyclic voltametry studies on the SAM covered surfaces/electrode

In this method, an inert SAM with a selective biofunctional agent is used to trap the heavy metals. In order to identify/detect the trapped heavy metals ions in the solution we have to develop a biosensor.

Task 3.2. Optimization of the electrochemical response of the electrode to the presence of heavy metals

These tests will help us to optimize the electrochemical response of the electrode by varying several parameters such as: protein concentration on the electrode surface, the concentration of heavy metal ions in the solution, pH, etc.

Forseen Impact

The final goal of the project is to demonstrate the possibility of using self assembled monolayers chemically coupled with target proteins to identify the presence of heavy metal ions.

The demonstration of a high selectivity by adapting nanotechnology techniques would open interesting perspectives in the whole domain of nanosciences and nanotechnology from biology to optoelectronic devices.

Possibility of developing a high sensitivity metal detection biosensor.

Interest and perspectives of collaboration

The interest of collaboration arises from the synergies and complementarity of the two laboratories. While LIRM is coming from a more biological background, CSSNT is coming from a surface science background, both having in common the interest in nano-medicine related research.

Also, direct collaboration will be done in phase with the COST Action TD 1002 goals. In particular we will present, during or at the end of the project, an FP8 proposal.

Study of new physics cases and preparation of SPIRAL2 experiments using the PARIS array



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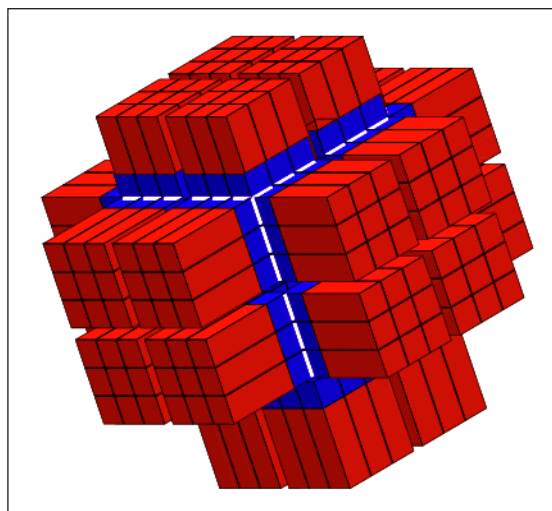


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The present project (Acronym: PARISNPC) is centred on the next generation gamma-ray detector array called PARIS (**P**hoton **A**rray for Studies with **R**adioactive **I**on and **S**table Beams) that will be constructed using recently developed $\text{LaBr}_3:\text{Ce}$ scintillating material. This scintillator features both a 65% higher photon yield than conventional NaI and has a fast decay component (25 ns) that is useful for timing measurements. Thus, the $\text{LaBr}_3:\text{Ce}$ material offers superior detection features that could be used for several applications in industry, medicine and basic and applied research. Although this scintillator cannot compete with germanium detectors in terms of energy resolution, their excellent efficiency and fast timing characteristics make $\text{LaBr}_3:\text{Ce}$ a necessary choice for many experiments and applications.

The general objective of PARISNPC project is to contribute to the development of PARIS multidetector and prepare its use in the experiments of interest for both the Romanian and French teams in the field of fundamental and applied research in nuclear physics.

PARIS is being developed mainly as an instrument for the SPIRAL2 facility that will be located at GANIL (Caen, France) and is one of the Research Infrastructures selected in the Roadmap of ESFRI (European Strategy Forum for Research Infrastructures). However, PARIS multidetector will have high modularity and mobility so that it will be used at other existing or future facilities. In particular it is well suited for experiments using gamma-beams at ELI-NP facility to be built in Magurele. Thus, the present project will focus on experiments to be performed with radioactive and neutron beams at SPIRAL2 and with gamma beams at ELI-NP. The use of new scintillator material, of modern digitization techniques and other innovative solution require extended R&D work to which the PARISNPC project will contribute. More specific, one of the objectives of the project is to study the PARIS capabilities to cope with high event rates and to resolve events separated by small time intervals, taking advantage of the fast response and excellent timing resolution, well below nanosecond, of PARIS compared to other existing gamma array. Currently PARIS collaboration involve 40 institutions from 17 countries and about 100 researchers, engineers and PhD students (see the collaboration web-site <http://paris.ifj.edu.pl> for details). PARIS collaboration was supported,



*PARIS proposed modular design
with clusters of 9 detectors.*

both on coordination and R&D activities, within FP7 SPIRAL2 Preparatory Phase project ended in March 2012. The FP7 CRISP (The Cluster for Research Infrastructures for Synergies in Physics) project, running till October 2014, also supports PARIS R&D work on digital electronics through one of his work-packages devoted to neutron and gamma detectors. This demonstrates that PARIS collaboration objective are fully integrated in the European strategies for R&D.

The above described activities of the project will be organized in four tasks:

T1: New experiments and simulation setting-up. This activity will be the first one to start in the project and, from justification of proposed experiments to the choice of theoretical models to be implemented in simulations, the work will involve equally the teams from CEA and IFIN-HH. First report of the project, at the end of first year, will present the results of this activity that will continue, to some extent, during next years, according to the needs of simulations and their outcomes.

T2. Simulation work. It will be performed based of the result of T1, starting by the mid of first year when the preliminary conclusions of T1 will become available. Simulation will use the Geant4 toolkit developed at CERN and adopted as basis for software development by PARIS collaborations. For the purpose of neutron and gamma background evaluation in NFS area the MCNPX code will be employed. The PARIS + ACTAR TPC simulations with Geant4 toolkit will be the responsibility of the CEA team and the remaining part will be done by IFIN-HH team. The results of the conceptual design and the physics simulations will be presented in the report at the end of the second year of the project.

T3. Pulse Shape Analysis. This task is mainly assigned to IFIN-HH. It will start during the first year of the project and will be based on measurement done with PARIS modules and associated digital electronics proving the signal shape to be analysed. This work will benefit also from advances on hardware and software solution proposed in the frame of FP7 CRISP project in the workpackages devoted to “High throughput detector data streaming” and “Innovative solution for gamma and neutron detectors”, in both of them being involved the Romanian team participating in the present project.

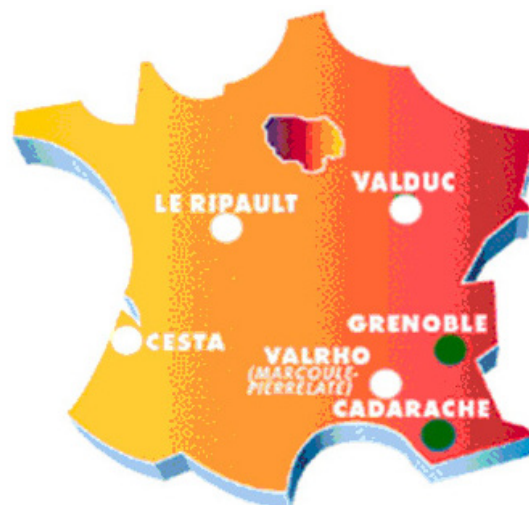
T4. Experimental work. The response of PARIS prototype, built by PARIS collaboration will be tested in various conditions, including with (stable) beams provided by a heavy ions accelerator. At the same time the PARIS demonstrator will start to be realised by PARIS collaboration and part of IFIN-HH budget will be used to contribute to its construction and preparation of first this use at SPIRAL2 which is expected to deliver the first stable beams in 2013. The work in this task will span all the three years of the project, with participation of both teams, and will be reported at the end of the project.

The results obtained in the project will be disseminated during the project duration through several international workshops/conferences and at least 1 peer-review article in an ISI ranked journal. Beyond that, the results of the project will be the basis of many future articles on the experiments to be performed using PARIS multidetector. The present project will open a long term collaboration between IFIN-HH, CEA/DSM and other partners toward PARIS array completion and its exploitation.



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