DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Chair:
Prof. Carlo Bottani

The thesis works that are presented in this Yearbook are very representative of the multi-disciplinary research activity performed within the context of the PhD educational and research program in Energy and Nuclear Science and Technology (STEN). The latter is specifically designed to provide the student with the state-of-the-art in a wide range of research fields related to:

· production, conversion and transmission of energy
· rational use of energy
· nuclear systems, nuclear fuel cycle, radioprotection
· application of ionizing radiations
· methods for safety and reliability analysis
· development of innovative materials for energy applications

The specific thesis discussed in this Yearbook are related to the PhD work of:

Astolfi Marco	An Innovative Approach for the Techno-Economic Optimization of Organic Rankine Cycles
Aufiero Manuele	Development of advanced simulation tools for circulating-fuel nuclear reactors
Bresciani Fausto	Experimental Investigation on Direct Methanol Fuel Cell Degradation
Carrozzo Paolo	Scanning Tunneling Microscopy and Spectroscopy of titanium and titanium oxide nanostructures on Au(111)
Cassetti Gabriele	Combined Risk and Exergy Analysis
De Servi Carlo Maria	Dynamic Modeling of Complex Energy Systems
Gatti Manuele	Multi-Objective Optimization of Novel CO2 Capture Processes for Gasification-Based Plants
Giostri Andrea	Transient effects in linear concentrating solar thermal power plant
Intini Manuel	A study of alternative desiccant cooling materials and equipment for low temperature trigeneration systems.
Lampitella Paolo	Large Eddy Simulation for Complex Industrial Flows
Lorenzoli Michele	A Novel Detection system for direct and high resolution spectrometry of intense neutron fields
Pini Matteo	Turbomachinery Design Optimization using Adjoint Method and Accurate Equations of State

Ponciroli Roberto	Development of a Model-based approach for studying the system dynamics and control of Gen-IV Lead-cooled Fast Reactor
Scaravaggi Stefano	Selective separation of minor actinides from spent nuclear fuel in homogeneous and heterogeneous recycling: extraction performances and speciation studies of chon hydrophilic ligands
Uccello Andrea	Development of nanostructured rhodium films for diagnostic mirrors employed in nuclear fusion systems

Radiation Science and Technology 24° cycle

CASATI Emiliano	BZT fluids for energy conversion systems

Their research and most significant results are presented in the following pages.

AN INNOVATIVE APPROACH FOR THE TECHNO-ECONOMIC OPTIMIZATION OF ORGANIC RANKINE CYCLES

Marco Astolfi - Supervisor: **Ennio Macchi**

1 Introduction

In the last twenty years the higher attention about climate change, global warming and externalities due to environment contamination and pollution have strongly encouraged the use of green technologies in power production field. ORCs (Organic Rankine Cycles) allow reducing the rate of consumption of fossil fuels and the emission of carbon dioxide by means of a wider exploitation of renewable energy resources like geothermal and solar energy. Furthermore ORCs are a reliable solution to increase the energy efficiency of any industrial plant where waste heat can be recovered for power production instead to be released to the environment. Thanks to their flexibility, they will surely play a relevant role in the world energetic scenario in future years.

2 Scope of the work

ORCs are based on the idea that the working fluid and the power cycle configuration should be selected according to the thermal level of the energy source, to the available thermal power and to the constraints related to key components like the turbine. In particular ORC are extremely attractive in all those application where the use of water as working fluid entails difficulties in components sizing leading to lower plant efficiencies and a less competitive LCOE (Levelized Cost of Electricity). Typical examples are application characterized by a small available thermal power or by low maximum temperatures sources. Despite their great potential, ORCs have been found a large market only in few fields, namely in biomass combustion CHP (Combined Heat and Power) plants and for the exploitation of hot geothermal brines, but their diffusion is still limited in many other applications and the potential upside of this technology is still large. The widespread use of ORC technology in new markets is strictly related to the availability of efficient components and numerical tools for the selection of the best combination of working fluid and plant layout. The aim of this thesis is to propose an innovative and comprehensive approach for the study of ORCs, their design and their optimization. A software named ORCO (ORC Optimization) has been implanted to reach the over mentioned goal.

3 Approach description

The approach proposed in this thesis is innovative from different point of view because it tries to overcome most of the limits highlighted in the methodologies present in literature. Limiting the study to single stream heat sources, the plant with the minimum LCOE is identify by means of the exhaustive investigation of different combinations of working fluids and cycle configurations. Each solution is fully optimized by a suitable algorithm. In order to obtain a reliable result, many different aspects have to be taken into account as briefly summarized below:

3.1 Working fluids thermodynamic properties: it is crucial to use suitable equations of state for the calculation of physical and thermodynamic properties in order to increase the accuracy and to guarantee a reliable estimation of component sizing and performances. ORCO is integrated with Refprop 9.1 which uses a state of the art database for pure fluids. In addition, it allows defining several UD (User Defined) mixtures but accuracy has to be previously checked comparing the numerical results with experimental VLE (Vapor Liquid Equilibrium) data from reference. A strong reduction of computational time and a higher stability of calculations in two phase region have been achieved thanks to Improvements on program routines.

3.2 Cycle configuration: several different plant layouts can be investigated, each one presenting different advantages and drawbacks depending on the thermal level of the heat source and the working fluid. with ORCO it is possible to investigate subcritical, supercritical, two pressure levels cycles and flash triangular plants. Any other cycle configuration can be added thanks to the modular structure of the code.

3.3 Expander efficiency: the expander is the key component for any ORC system, for big power plants usually axial-flow turbines are adopted while for small power output, positive displacement devices are suggested. In ORCs it is crucial to link the actual efficiency of the expander to the thermodynamic properties of the fluid and to the cycle layout. For axial flow turbines an extensive numerical activity has been carried out optimizing several hundred turbines and comparing the results on the base of similarity theory. Efficiency correlations are proposed for single stage, two stage and three stage turbines at optimized rotational speed in wide ranges of volume ratio and machine radial dimension. For screw volumetric expanders a correlation of efficiency has been derived by analyzing maps of performances provided by producers.

3.4 Cost correlations: an extensive bibliographic research has been carried out with the aim to define a suitable cost correlation for each component commonly adopted in ORC field. A detailed analysis is performed for Shell&Tube heat exchangers and axial flow turbines since they are the most expensive components for ORC. In particular the cost correlation for turbines is quite innovative and can be used to estimate the cost of machines working with organic fluids and so characterized by a limited number of stages and high stage volume ratios and steam turbines where usually a higher number of stages is adopted.

4 Test cases

Different analyses have been successfully carried out with the proposed approach, investigating some of the most interesting ORC applications. A detailed study is proposed for geothermal energy exploitation where supercritical, subcritical and two pressure levels cycles are compared. Two different analyses are considered: the first one with the aim to maximize power production while the second one oriented to the minimization of overall LCOE. The most promising solution are highlighted leading to the definition of criteria for the pre-selection of suitable working fluids and cycle layouts. In particular the results underline the highest performances attainable with supercritical cycles and two pressure levels cycles compared to the subcritical ones. From a techno-economic point of view, instead, all the cycle configurations when properly optimized, reach a comparable LCOE for a relatively small number of fluids suggesting general rules for the selection of working fluid on the basis of reduced parameters. Another study has been performed comparing ORC and steam Rankine cycle in waste heat recovery application from big cement production plants; a field characterized by a relatively high available thermal power and a high temperature of the hot source. These applications are part of the so called "grey zone" where it is not easy to define if organic fluids can actually compete against water which shows higher film transfer coefficients, and so less expensive heat exchangers, but a larger turbine. Finally two studies are carried out investigating (i) the potential of mixtures for biomass CHP plants where the temperature glide in phase transition can be advantageous since allow increasing the power output and (ii) the use of volumetric screw expanders for small size applications.

5 Conclusions

A comprehensive methodology for the analysis of ORCs is proposed and a software, named ORCO, is realized in order to face all the difficulties related to the design and the optimization of ORCs. The numerous innovative aspects implemented into the code allow performing broad spectrum analysis by considering a reliable efficiency for key components and suitable economic evaluations. This approach has been tested on different test cases proving the affordability of the systematic procedure implemented. From these studies interesting conclusions about the general criteria of selection for both working fluid and cycle layout are highlighted.

DEVELOPMENT OF ADVANCED SIMULATION TOOLS FOR CIRCULATING-FUEL NUCLEAR REACTORS

Manuele Aufiero - Supervisors: **Antonio Cammi, Lelio Luzzi**

Introduction

Molten Salt Reactors (MSRs) are characterized by a unique distinguishing feature: the presence of a liquid nuclear fuel. This peculiarity may lead to intrinsic improvements in the fuel cycle closure and reactor safety enhancement. On the other hand, it represents one of the most challenging aspects for reactor design, analysis and operation. Recently, renewed interest has grown in different countries on the MSR technology, focusing on both thermal- and fast-neutron reactors, for the development of breeder, converter or incinerator systems. In particular, the Molten Salt Fast Reactor (MSFR), a new reactor concept developed in the framework of the EURATOM EVOL (Evaluation and Viability of Liquid Fuel Fast Reactor System) Project, has been selected as the reference circulating-fuel reactor in the framework of the Generation-IV International Forum.

The context of the present PhD thesis is the research domain oriented towards the development and assessment of advanced modeling and simulation tools for circulating-fuel nuclear reactors. The MSFR is studied in parallel to the process of development and assessment of the different simulation tools, focusing on those aspects that are more constraining for this technology and are currently studied with a lesser degree of accuracy.

Core materials evolution

The adoption of on-line reprocessing schemes offers several advantages but may lead to some problems due to the necessity of handling highly radioactive streams. For this reason, accurate depletion calculations are highly desirable for MSR systems. Unfortunately, the presence of on-line reprocessing prevents the adoption of commonly available fuel burn-up codes. In the first part of the thesis, the Monte Carlo reactor physics and burn-up code Serpent has been extended with the capability to catch the effects of on-line fuel reprocessing and to allow realistic simulations with a continuous reactivity control algorithm. On-line fuel reprocessing is explicitly introduced in the system of burn-up equations by adding effective decay and transmutation terms for the different nuclides, representative of fission products removal and fuel injection. In this way, the modified equations of isotopic evolution can be handled adopting common efficient techniques for the matrix exponential computation. The extended Serpent features a reactivity control that allows keeping the multiplication factor close to 1 during the whole simulation. This is performed by continuously adjusting the fissile-to-fertile ratio in the feed material, simulating the operational reactor control, and allowing a correct estimation of the main reactor breeding parameters. The developed tool is adopted for the fuel-cycle analysis of the MSFR. Results show that the handling of salt extracted from the core can be problematic due to decay heat and emission of neutrons and high energy gammas. The contribution of the main (n,α) reactions responsible of helium production in the structural materials has been investigated as well, confirming that irradiation induced damage of structural components is a relevant issue for the deployment of the MSFR technology. A sensitivity analysis to the cross-sections data libraries is presented, showing the large impact of the uncertainties in the U-233 capture cross-section on the reactor breeding performance estimates.

Multiphysics modeling

Neutronics/thermal-hydraulics coupling for reactor analysis is often performed by means of classical "coupled-codes" techniques. This approach has proved to be inadequate in cases where an intimate coupling between the physics and the stiffness of the equations call for the adoption of implicit, higher-order time integration schemes and a CFD solution of the fluid flow. Often, the non-linearities due to the coupling are not fully resolved, possibly reducing the overall accuracy. In MSRs, the presence of strong interactions between the different phenomena requires the adoption of suitable modeling approaches.

In the second part of the thesis, a specific solver has been developed, adopting the multiphysics toolkit OpenFOAM. The modeling efforts are focused on the implementation of coupling techniques, and the adoption of strategies for the reduction of computational requirements. The constitutive equations of the main physical phenomena governing the reactor behavior are discretized and solved adopting standard finite-volume techniques and efficient linear algebra tools available in OpenFOAM. Namely, the equations involved in the multiphysics solution are the time-dependent neutron diffusion, the balance equations for delayed neutron and decay heat precursors, and the incompressible Reynolds-Averaged Navier-Stokes equations for the solution of the turbulent fluid flow. The main purpose of the proposed model is to serve as fast-running computational tool in the phase of design optimization of the MSFR core and fuel loop components. The capability of performing accurate simulations on detailed full-core realistic 3D geometries is not available in previous tools, which are limited to 2D simplified geometries. This feature is shown to be a mandatory requirement for core design optimization and analysis of asymmetrical accidental scenarios. The capabilities of the model have been assessed against Monte Carlo simulations and results from previously available multiphysics tools. An unprotected single pump failure MSFR accidental scenario is presented in the thesis. The results of the simulation give useful indications for the ongoing activity of core shape optimization.

Effective delayed neutron fraction

The effective delayed neutron fraction (β_{eff}) is an important reactor kinetics parameter. The contribution of delayed neutrons is of primary importance for the safe control of any nuclear reactor. The traditional definition of β_{eff} involves the calculation of both the forward and the adjoint solution of the neutron transport equations, which makes its accurate calculation by means of continuous energy Monte Carlo codes a challenging task, even for static-fuel reactors. In circulating-fuel systems, the motion of delayed neutron precursors complicates the calculation of the effective delayed neutron fraction and prevents the adoption of commonly available neutron transport codes.

In the last part of the thesis, three methods are presented for the calculation of the effective delayed neutron fraction in circulating-fuel reactors. The first approach involves an analytical formula for the β_{eff} correction, which explicitly takes into account the in-core spatial importance effect and allows for radial redistribution of the delayed neutron precursors that re-enter in the core. The second method features the simultaneous solution of the equations of neutron diffusion and precursor convective and turbulent transport. This approach involves the solution of the forward and adjoint eigenvalue problems for arbitrary geometries based on detailed spatially-dependent velocity fields. A Monte Carlo-based approach is also developed through the extension of the Monte Carlo code SERPENT, and involves the tracking of precursors according to an input velocity field. The effective delayed neutron fraction in circulating-fuel conditions is then calculated adopting the Iterated Fission Probability method. The three approaches are compared in the MSFR case, showing a good agreement and highlighting that commonly adopted one-dimensional approaches, not featuring spatially-dependent adjoint-weighting, overestimate β_{eff} up to 20%.

# EXPERIMENTAL INVESTIGATION INTO DIRECT METHANOL FUEL CELL DEGRADATION

Fausto Bresciani - Supervisor: **Renzo Marchesi**

Direct Methanol Fuel Cells is a promising technology for portable and uninterruptible power supply. Among the technical issues that still hinder the commercialization of this technology, there are methanol crossover from anode to cathode resulting in a waste of fuel and severe performance degradation. DMFC degradation presents two components: a permanent (irreversible) degradation and a temporary (reversible) degradation that can be recovered by interrupting the operation. However, despite some DMFC permanent degradation mechanisms are proposed in the literature, the origins of DMFC temporary degradation are not clear. Moreover no work provides systematic analysis on mass transport phenomena evolution during the degradation and the permanent degradation is not quantitatively attributed to the DMFC components. This work aims to experimentally investigate DMFC temporary and permanent degradation in order to improve degradation mechanisms knowledge and to develop preliminary Accelerated Stress Tests (AST).
The steady state (continuous) operation of a DMFC shows very strong performances degradation that cannot be compatible with a real application but that is mainly

recoverable. For this reasons, DMFC are usually operated by means of operating strategies (cycles) that can be optimized in order to reduce the performance decrease in time. The operating strategies allow to reduce the temporary degradation and, through a comparison of different cycles, a optimized operating strategy for the DMFC degradation tests is adopted for the DMFC degradation tests performance. Furthermore in-operando diagnostic tools have been tuned in order to improve the characterization of both temporary and permanent degradation mechanisms. Different temporary degradation mechanisms have been experimentally characterized such as platinum oxides formation at the cathode electrode, dehydration of the cathode electrode and hydrogen production at the anode during oxygen starvation that occurs in the operation interruptions. A mechanism for the anode temporary degradation, for the first time in the literature, is proposed and validated thank to Electrochemical Impedance Spectra (EIS) and mass transport measurements; the anode recoverable performance loss is due to the accumulation of CO_2 in the anode electrode during the operation resulting in a decrease of methanol and water concentration; the CO_2 can be

removed during the interruption in the operating strategy and this mechanism determines a progressive reduction of the methanol crossover during the DMFC operation.
The mass transport phenomena has a fundamental role on DMFC performance and degradation and the Gas Diffusion Layer, a component that controls the transport mechanisms, has been previously investigated ex-situ and, later, the effect of such component on DMFC performances and degradation has been evaluated. Water diffusion and permeation through the GDL are quantified and the effect of a preliminary Accelerated Stress Test for GDLs on the mass transport properties is evaluated. From the characterization of the effect of the GDL hydrophobic properties on the DMFC performances, the lower the GDL hydrophobicity and the higher the methanol concentration in the anode electrode; this leads to a gain in anode performances and a strong decrease in the cathode performance due to both the increase of methanol crossover and the water flooding of the cathode electrode that reduce the oxygen concentration at the cathode electrode.
The experimental investigations on DMFC temporary degradation mechanisms allows to define a procedure

for temporary degradation minimization that aims to provide a reliable quantification of DMFC permanent degradation, which is of fundamental importance for the comparison of industries and laboratories data.
A long-term test of about 1100 hours has been performed on a DMFC with continuous in-operando diagnostic thank to electrochemical and mass transport measurements; the DMFC works using the optimized operating strategy. The performance degradation reported in figure 1 shows the two different degradation components and the permanent degradation is evaluated during the operation interruptions. The cathode Electro-Chemical Surface Area (ECSA) is halved after the degradation tests as reported in figure 2; cathode is responsible for 65% of the permanent degradation while anode is responsible for 34% and membrane degradation is negligible. Post-Mortem measurements performed by research project partners report a increase of catalyst particle size due to Platinum dissolution and re-deposition and Ruthenium crossover from the anode to the cathode.
Preliminary Accelerated Stress Tests (AST) have been designed and tested with the goal of the simulation of a long-term
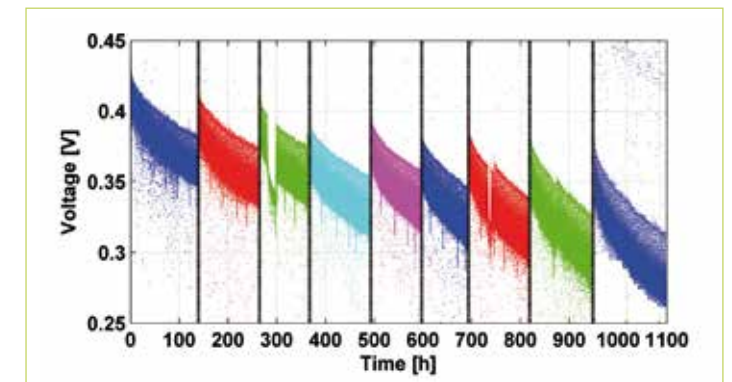
tests in order to reduce the degradation tests duration; however the AST aims to be representative of the permanent degradation that a DMFC would suffer after a long-term test and, for this reason, it should amplify the same degradation mechanisms that occurs during the real DMFC operation.
The designed AST aims to accelerate the cathode degradation by exposing the cathode catalyst to continuous formation and reduction of oxides, cycling between high and low potentials in order to promote the cathode platinum dissolution mechanism. The halving of the ECSA has been obtained in 300 hours meaning a more than 3 times Acceleration Factor for the cathode active surface area loss.

1.
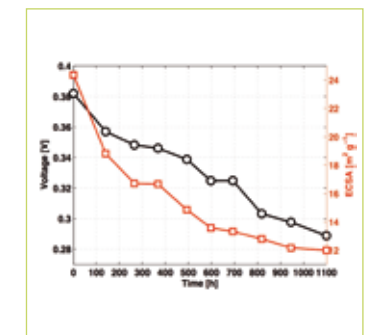
2.

SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF TITANIUM AND TITANIUM OXIDE NANOSTRUCTURES ON AU(111)

Paolo Carrozzo - Supervisor: **Prof. Andrea Li Bassi, Dott. Carlo Casari**

The main topic of my thesis work deals with the study of nanostructured surfaces of metal oxides by means of Scanning Tunneling Microscopy and Spectroscopy. This study is aimed at extending the basic knowledge of titanium oxide surfaces and nanostructures, particularly with reference to their morphological and electronic properties at the nanoscale.

Titania (TiO_2) is one of the most relevant strategic materials in many technologically important areas, like heterogeneous catalysis, photo-assisted oxidation, optical and photovoltaic devices. Nano-dimensional TiO_2 shows surface mediated structural, chemical and electronic properties different from those of the most common bulk polymorphs. Therefore a detailed knowledge of the surface properties of the nanodimensional TiO_2 phases is crucial to exploit the full potential of these nanostructures. In order to achieve this purpose, it would be suitable to realize a model system in which titanium oxide clusters should be deposited on a model surface. A possible choice is the Au(111) surface, because of its ease of handling, its chemical inertness and the fact that its "herringbone" surface reconstruction may serve as a well-defined template for ordered growth of nanoparticles.

There are many techniques for surface analysis that allow to characterize these model systems: one of the most powerful is Scanning Tunneling Microscopy (STM), a particular scanning probe imaging technique. By means of a tip that scans over a surface at a sub-nanometric distance, a tunneling current is generated when a bias voltage is applied. Usually, this effect is exploited under ultra-high vacuum conditions in order to avoid surface contaminations (UHV). Since the tunneling current varies exponentially with respect to the distance between the tip and the sample, the effective interaction area is reduced to a few atoms of the tip, allowing in some special cases to reach the atomic resolution. The extremely high achievable resolution is widely exploited in the investigation of surfaces and nanostructured systems. In this way, STM is now universally recognized as a fundamental tool for the investigation of surfaces on the nanometric and atomic scale.

Besides its capability of acquiring images that represent morphological properties of the topmost surface atomic layer of metals and semiconductors, many other important properties can be extracted from an STM measurement. The tunneling current depends on the tip and sample electronic structures, thus allowing the possibility of acquiring local information about surface electronic properties. In particular, by measuring the tunneling current with respect to the applied voltage, this technique can also be used also to perform the so-called Scanning Tunneling Spectroscopy (STS). STS can provide information about the electronic local density of states (LDOS) with extremely high spatial resolution. Generally, these measurements are carried out at low temperature (LT) in order to reduce thermal drift and tip instability. As a first approximation, it is possible to interpret the current as an energy convolution between tip and sample electronic states weighted by a transmission coefficient that is characterized by an exponential behavior with the applied voltage. Therefore, the complexity of the STM-STS techniques is mainly due to the fact that the results also depend on the morphological and electronic properties of the metallic tip employed in the experiments. In this framework, a strong effort is still required to fully understand and minimize the tip effects.

In the light of these considerations, we focused on the STM-STS investigation of the structural and electronic properties of metal oxide surface and interface, especially titanium oxide nanostructures. The approach used here permitted to accomplish many interesting results on the fundamental knowledge of the material properties at the atomic scale, which is a crucial step on the way to the design of materials with engineered properties that could be employed in many applications (e.g., catalysis and photovoltaics). To achieve this goal, we adopted a two-fold methodology.

In the first part, we focused on the study and the development of the STM-STS techniques, in particular by producing bulk tip with novel materials. We have implemented a simplified method to produce bulk molybdenum tips and we have investigated their potentiality as STM probes. The lateral sensitivity of these tips allowed us to image Si(111) surface with atomic resolution resolving routinely the rest atoms of its reconstruction. On Au(111) surface, these tips have also been proved to be capable of STS measurements, revealing peculiar differences with respect to other tips. Mo tips have been successfully employed for original measurements of surface nanostructures, e.g. Ti and TiO_x on Au(111). Furthermore, the method used for the fabrication of Mo tips is versatile and it could be extended to other metals, such as Co.

The purpose of the second part of this work is to characterize the morphological and electronic properties of Ti and TiO_x clusters deposited on Au(111). First, we focused on titanium nanocluster properties before the oxidation. We performed a detailed STM/STS study of the growth of titanium on the Au(111) reconstructed surface. The initial preferential nucleation of Ti islands at the elbows of the herringbone reconstruction is accompanied by out-of-elbow nucleation starting from the lowest coverage investigated. Increasing the coverage, the island size increases with coalescence starting at a value that is retarded with respect to other systems, such as Pd, while second layer features appear before the first is completed. Ti islands are characterized by a peculiar granular structure (found also for the second layer) suggesting that islands are indeed made of assembled clusters (grains).

LT STS measurements revealed that Ti islands are characterized by three dominant electronic features around Fermi energy, whose energy positions do not change as a function of coverage. dI/dV maps reveal the presence of some substrate regions with electronic features similar to Ti islands, and local STS spectra of these regions show a strong correlation with those revealed for Ti islands. Such observations and the modification of the Au(111) surface Shockley state suggest an important interaction between Ti and the Au surface. After this experiments, we have performed a STM/STS study on the TiOx thin films grown on Au(111) reconstructed surface. We identified five different structures: in order, pinwheel, triangular, honeycomb, row and needle phase. Two different hexagonal commensurate phases could constitute the first layer of this system. Below 0.8 ML, reconstructed pinwheel appears at first as single crystallites that, as the coverage is increased, begins to coalesce until they form an uniform film whose topography can be described as a Moiré pattern. After 0.8 ML, this phase coexists with a honeycomb structure that reveals a lower Ti density and a Ti_2O_3 stoichiometry. 3D shaped structures could grow on top of this first layer, such as triangular crystallites, row islands and needle clusters. While triangular phase reveals a hexagonal symmetry, a rectangular unit cell characterizes both the other two phase.

Finally, we performed LT STS measurements on all these phases, except for the needle structure because of its infrequency. While 3D clusters are characterized by a gap of different width, pinwheel and honeycomb reveal different electronic features. Indeed their spectra do not show a gap but a series of characteristic peaks that, especially for the pinwheel, seem to depend on the extension of the film. Furthermore, contrary to the case of Ti/Au(111), the Au Shockley peak does not reveal any significant modification with respect to the case of a clean surface, suggesting a more weak interaction between film and substrate compared with the system before the oxidation.

COMBINED RISK AND EXERGY ANALYSIS

Gabriele Cassetti - Supervisor: **Prof. Emanuela Colombo**

The Combined Risk and Exergy Analysis (CRExA) is an analytical model aiming at finding the correlation between inefficiency sources of an energy system or process and the direct impact that these have on human health and environment and minimizing the associated risk. The model integrates a risk analysis of the system with an exergy analysis. Exergy analysis is an effective method for: a) combining and applying the conservation of mass and conservation of energy principles together with the Second Law of Thermodynamics for the design and analysis of energy systems, b) improving the efficiency of energy and other resource use, c) revealing whether or not and by what extend it is possible to design more efficient systems by reducing the inefficiencies in existing systems, d) addressing the impact on the environment of energy and other resource utilization, and reducing or mitigating their impact.
The CRExA model combines exergy and risk analyses for improving efficiency and safety of energy systems by reducing the associated risk once the influence of irreversibility is identified via a thermodynamics analysis. Indeed irreversibility can increase resource consumption in processes and lead to a quantifiable effect on the risk associated to the system. The integration of the two analyses is performed according to the Thermoeconomic frame. Thermoeconomics is defined

as a technique that combines economic and thermodynamic analysis by applying the concept of cost to exergy, in order to provide the analyst with information not available through conventional energy analysis and economic evaluation. Another relevant definition is "exergy aided cost minimization". In this sense, the concept of exergy is used in the CRExA model as a measure for accounting the social cost in terms of risk to human health, and the thermoeconomic approach provides the relevant information on the irreversibility influence on cost. Hence, using risk analysis as objective function on the theoretical structure of the Thermoeconomic analysis can lead to the identification and quantification of such contribution.
Assuming the *risk* of the system, evaluated according to risk analysis methodology, as a cost for the society, this approach can produce an information equivalent to what Thermoeconomics does for monetary cost, where the *cost* is represented by the *risk* to "accept" in order to benefit from the product of the system (e.g. electricity, gas, heat for energy systems). The model hence is conceived to identifying the elements of highest impacts in terms of damage to human health. In this manner, it can be used to delineate specific indications for the system design and the identification of the

safety measures required by regulations.
The *exergy costing principle* is expressed in terms of risk and the *cost balance* is converted in a *cumulated risk balance*, obtained performing a quantitative risk analysis. The *exergy costing principle* can be therefore defined for the product as:

$$\dot{R}_p = r_p \dot{E}_p \qquad (1)$$

The complete model is defined by the following system of equations to be applied to the k-th component of the system.
Being the risk n expressed in [events · y^{-1}], the mathematical symbolism $\dot{R}$ is used. The system is hence:
the exergy costing equation of the product in terms of risk (2a)
the exergy account for component k (2b)
the cumulated risk account in component k (2c)

In Eq.(2a), the exergy costing is defined in terms of risk: this assumption is here made only for the product $\dot{E}_p$ and the risk $\dot{R}_p$ to produce it. This assumption is possible since risk and exergy balance, connecting $\dot{E}_D$ and $\dot{E}_p$, are demonstrated to be somehow correlated through the parameters of the system.
It is worth mentioning nonetheless that Eq (2a) does not state that R$_p$ is dependent from the specific exergy of $\dot{E}_p$, but only that the risk R of producing a product is allocated to the

$$\begin{cases} \dot{R}_P = r_P \dot{E}_P & \text{the exergy costing equation of the product in terms of risk (2a)} \\ \dot{E}_{F,k} = \dot{E}_{P,k} + \dot{E}_{L,k} + \dot{E}_{D,k} & \text{the exergy analysis of component } k \text{ (2b)} \\ \dot{R}_{P,k} = \dot{R}_{F,k} + \dot{R}_k & \text{the cumulated risk account in component } k \text{ (2c)} \\ \dot{R}_{F,k} = \sum_{\delta=1}^{\gamma} \dot{R}_{k-\delta} & (2e) \end{cases}$$

product itself . Eq. (2b) is the exergy balance at component k , where $\dot{E}_{F,k}$ is the exergy input (Fuel) in component k, $\dot{E}_{P,k}$ is the exergy output (Product), $\dot{E}_{L,k}$ is the eventual exergy loss and $\dot{E}_{D,k}$ is the exergy destroyed in component k. The risk R of the product in Eq. (2c) is given by two contributions : $\dot{R}k$ is the result of the risk analysis performed on k-th component (Eq. 2d) and $\dot{R}_{F,k}$ is a the cumulated risk associated to the intermediate products to produce P in component k, which hence is the result of the risk analysis performed on the δ upstream components (Eq.2e). Finally it is possible to evaluate the specific risk of the product of k:

$$r_{p,k} = \dot{R}_P / \dot{E}_{P,k} \qquad (3)$$

The calculation of the $\dot{R}_p$ function is necessary for the implementation of the model and the evaluation of specific risk r$_p$ is the ultimate parameter to minimize.
It is worth mentioning that rp is not necessary a constant and may depend on the same parameters on which $\dot{E}_p$ and $\dot{R}_p$ depend.
The model of Eq. (2) is a starting structure and it presents naturally some points strength which might give a significant contribute to classical risk analysis, and some points of weakness.
The first point of strength of the model relies in its formulation: connecting the risk associated to a system to its thermodynamics through the thermoeconomic

structure, **the model can help identifying configurations that are intrinsically safer than others**. Intrinsically safer means that a configuration is safer compared to another all the protection systems being equal. For an energy system designed to produce exergy (e.g. thermal plants, oil and gas processes, etc.) the use of the model might supply an information on the balance between Product Cost and Social Cost which **is more objective and independent on political choices**.
As Thermoeconomics allows the calculation of costs associated to exergy loss, the model might help **to identify processes and components of the system where more effective improvements can be set and focus on them for improving the safety of the whole system**, accounting however for dependencies among components: as Thermoeconomics allows the calculation of costs associated to exergy loss, the model allows the calculation of risk associated to exergy loss, though with some differences.
The complementary application of traditional Thermoeconomics and CRExA allows the **evaluation of the monetary cost of risk avoided**.
On the other hand some weakness points in the actual formulation can motivate to develop and improve the model. **The formulation is not yet completed for systems**

not designed for power generation . The application is at the current stage of its development limited therefore mainly to power systems, and this represents a limitation since risk analysis can be applied on every process and activity.
In pure Thermoeconomics the definition of Fuel is more linear, since the distinction between $\dot{C}_{F,k}$ and is clear, as cost related to exergy input and investment respectively. **In CRExA formulation, the distinction between $\dot{R}_{F,k}$ and $\dot{R}_k$ is more subjective**. At level of the single component the definition of the risk related to Fuel needs to be accurately detailed to perform "risk" accounting and evaluate the risk allocated on exergy losses and destruction.
The definition of risk becomes more complete as long as more variables are included, such as the vulnerability of the target, the distance, the relative localization etc. **The inclusion of additive variables, even though it provides a more accurate and realistic perception of the risk associated to a system, weakens the relation with the thermodynamics of the system**. The application of CRExA is therefore suggested (limited) to local risk index.
Finally, the uncertainty representation in CRExA can lead to reducing the level of subjectivity of risk calculation and obtaining a value closer to the real perception of risk.
The model has been proposed to scientific community and two papers have been published on it.

DYNAMIC MODELING OF COMPLEX ENERGY SYSTEMS

Carlo Maria De Servi - Supervisors: **Stefano Consonni**

This thesis is the result of my research experiences on physically based dynamic modeling of energy systems. In this framework, I focused on two different research fields: 1) the analysis of the dynamic behavior of waste or biomass combustion in grate furnaces and 2) the dynamic modeling of an absorption packed column for CO_2 removal from syngas streams. The latter topic stems from my involvement in the "CO_2 Catch-up" research project, a R&D program carried out by the Vattenfall energy company to demonstrate the technical reliability of carbon capture technology into IGCC plants. The technological option considered to separate CO_2 from the syngas is physical absorption by means of a solvent, specifically the Selexol process. One of the main objectives of the research activity was the development of modeling tools to perform the dynamic simulation of a CO_2 capture plant. In fact, the combination of the CO_2 capture process with a very complex plants such as IGCCs can lead to challenging problems as far as dynamic operations are concerned. To support the research, Vattenfall put into operation a CO2 capture pilot plant at the Buggenum IGCC power station, in the south of Netherland. Thus, the models I developed for the

CO$_2$ absorber were validated against experimental data collected at the pilot plant. Such a research experience allowed me to acquire knowledge about the concepts and the issues related to the dynamic modeling of energy systems, and to get expertise with the simulation tools dedicated to this kind of problems. The other research field of my PhD studies was dynamic modeling of waste/biomass combustion in grate furnaces. I chose this topic essentially for two reasons. First of all, in spite of the several modeling efforts of the last decade, there is still a lack of models for waste or biomass combustion expressly designed for dynamic simulation. In fact, it is not casual that, at present, there are only few waste to energy plants that feature advanced control systems. Second, there is a growing interest by the companies of this sector in improving the operating performance of the plants, owing to more stringent environmental regulations, the reduction of incentives and the need to reduce the waste disposal fee. In order to meet these objectives, the managers of WTE plant are trying, inter alia, to increase the operating performance of the boilers, by improving the combustion control system, by installing new devices (e.g.: infrared cameras,

acoustic sensors to map the temperature in the flue gas streams) and by enhancing the skills of the operators. A dynamic model can be an invaluable aid for the fulfillment of such actions. In fact, the complexity of the phenomena involved and the unsteady nature of combustion, caused by the continuous variation of the properties of the fuel (e.g. chemical composition, humidity content, heating value), make very difficult to understand the different input/output relations between the process variables with heuristic approaches. However, these characteristics of the combustion process imply also that the definition of a first principles model is a very challenging task. For this reason, the first part of the modeling activity focused on the development of a one-dimensional model to simulate the dynamic behavior of waste or biomass combustion in so called "pot furnaces". In these batch reactors solid fuel is piled on a stationary grate and it is ignited from the top by a thermal radiation source, while air is fed from the bottom of the reactor and flow upwards through the solid bed. Such experimental rigs are used especially in the academic community to investigate combustion in packed beds. In this way, I could exploit for modeling the experimental data
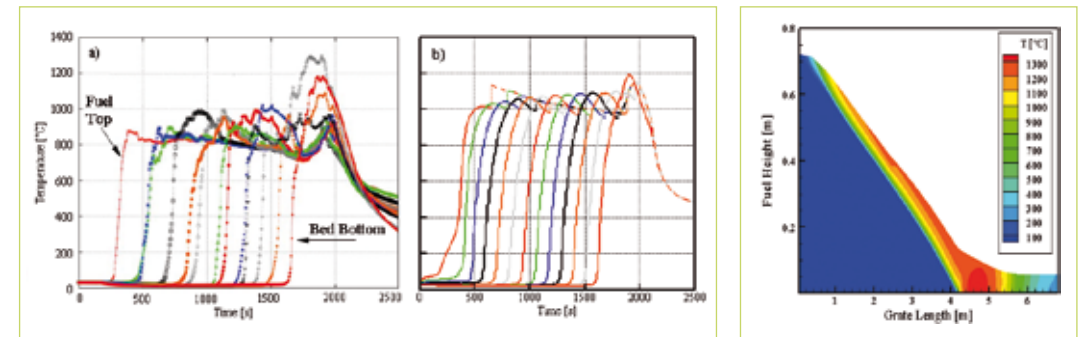
1. Pot furnaces experiments - variation of temperature inside the fuel bed during combustion, (a) experimental measurements – literature data, (b) model predication

2. Temperature distribution of the fuel bed along the gratePerformance Trends

collected during laboratory tests, where the fuel composition is known and more process parameters are monitored and measured in reliable way than industrial facilities. An example of these data is reported in Figure 1a, that shows the variation of temperature at various heights of a packed bed of wood chips during the experiment. Steep temperature gradients are observed to occur progressively from the bed top to the deeper layers of the fuel bed. In fact, as the combustion proceeds the ignition front propagates downward. Figure 1b reports instead the simulation results of the 1D model, which demonstrate that the model predicts with adequate accuracy the evolution of temperature in the solid phase during combustion, certifying also the correctness of the developed

code.
The 1D model was, then, adapted and extended in order to predict the behavior of waste combustion in a real grate furnace. Such furnaces are so called because at the bottom of the combustor there is a mechanical component – the grate – which is designed to support, transport and eventually mix the waste during combustion. Oxygen for the combustion processes is provided by the underfire air or primary air injected below the grate. The fuel bed is also not stationary, but it moves through the combustion chamber towards the ash pit. Thus, it is necessary to employ a two-dimensional model in order to describe the fuel conversion process. Such a simulation tool is derived by using as base model the 1D model previously described. In

this task, some approximation are inevitably introduced to obtain an accurate, yet manageable, process model and simulator. Thanks to the collaboration with the company that manages the WTE plant of Piacenza, Tecnoborgo Spa, the developed simulator was tested in relation to a real operating plant. In particular, the dynamic model was used to determine a temperature map of the fuel bed for a preset distribution along the grate of the underfire air (see Figure 2). These simulation results are very useful for the managers of the plant, because they want to integrate in the control strategy of the boiler the information provided by an infrared camera that monitors from the ceiling of the furnace the temperature of the surface of the waste bed.

MULTI-OBJECTIVE OPTIMIZATION OF NOVEL CO$_2$ CAPTURE PROCESSES FOR GASIFICATION-BASED PLANTS

Manuele Gatti - Supervisors: **Stefano Consonni, Emanuele Martelli, Federico Viganò**

1. Background, motivation and context

Coal to Liquids (CTL) as well as Coal to Substitute Natural Gas (Coal-to-SNG) and Integrated Gasification Combined Cycle (IGCC) plants take advantage from the conversion of a relatively inexpensive and abundant, fossil fuel like coal into a clean synthetic gas, to produce either liquid fuels, chemicals or electricity.
According to a mid-term perspective, in an electricity market characterized by restrictions on CO$_2$ emissions, pre-combustion Carbon Capture and Storage (CCS) is likely to become a standard feature of IGCC power plants.
For similar reasons, as far as the production of "low-carbon emissions" liquid fuels is concerned, the conversion of coal into synthetic liquids with CCS (capturing the carbon in excess to the synthetic fuel content) seems one of the most promising and viable options to provide an alternative to oil derived fuels, capable of being competitive in terms of economics, environmental impact and energy security, especially when high oil prices are envisaged.
The subject of this work is the development and optimization of novel pre-combustion CCS options suitable for such gasification-based plants.

2. Research goals

The main objectives pursued by this research are the following:
· Develop and efficiently solve a detailed model of Selexol and Rectisol identified as benchmarks for Acid Gas Removal (AGR) in a gasification-based plant.
· Find, optimize and patent novel low temperature CO$_2$ removal configurations featuring either phase-change or solvent-based absorption or a combination of both.
· Set up a strategy to simultaneously perform the heat integration as well as the selection and design of the required utilities.
· Formulate and solve the multi-objective optimization problem with respect to the two conflicting objectives, maximum CO$_2$ removal rate and minimum equivalent electric consumption, while taking into account the effect of design parameters, such as the minimum temperature difference between hot and cold streams, on the capital cost, via sensitivity analysis.

3. Methodology and tools

A minimization of the energy penalty for CO$_2$ capture could come both from an improvement at the level of the flowsheet and from the optimization of operating conditions. The following approach has been pursued:

A. the most interesting technologies are selected on the basis of a preliminary screening; for each of the evaluated processes, the thermodynamic model, namely the Equation Of State has been properly calibrated by solving a Matlab optimization problem, and the most appropriate flowsheet arrangement is defined by means of Aspen Plus process simulation and pinch analysis
B. for each given scheme, the optimal operating conditions are identified through multi-objective numerical optimization of the detailed flowsheet defined at step A.

The multi-objective optimization strategy is more general from an engineering point of view than the classical single-objective one, and it is preferred when dealing with scenario analyses where the conflict between two objectives depends on key, unpredictable, input parameters. This is the case of this study, since the CO$_2$ tax, which affects significantly the choice of the optimal CO$_2$ capture rate represents a crucial, uncertain parameter.

4. Development of novel pre-combustion CCS processes

A detailed heat integration analysis supported by the application of process integration principles, led to the definition of a modified-Rectisol scheme, showing substantially better performance than the classical layout. By means of the same approach, two additional novel processes, developed and patented as a result of a research collaboration pursued by the author and his supervisors together with BP (British Petroleum, which owns the patents) have been identified: TurboCapture, based on CO$_2$ separation via partial condensation, and Hybrid, which is a synergy of TurboCapture and modified-Rectisol.

4.1. Modified-Rectisol

The modified-Rectisol version differs from the conventional Rectisol for the following features: (i) the CO$_2$ desorption section instead of including a flash regeneration plus an H$_2$S concentrator consists of a single desorption column exploiting CO$_2$ flashing, H$_2$S re-absorption and auto-refrigeration; (ii) the methanol regeneration section is split in two stages in order to minimize the exergy destruction within the reboiler.

4.2. TurboCapture

TurboCapture exploits the high volatility difference between CO$_2$ and non-condensable fuel species present in the syngas to separate an almost pure CO$_2$ stream via partial liquefaction. Therefore, this option takes advantage from a proper combination of mechanical compression and refrigeration in one or multiple separation steps to remove the CO$_2$ from the syngas stream.

4.3. Hybrid process

Starting from the inherent drawbacks of the modified-Rectisol and TurboCapture, i.e. the high solvent circulation rate and refrigeration duty as well as the limited separation capability respectively, an arrangement with the following features has been identified: (i) the H2S absorber of the classical Rectisol is kept unchanged, even though its operating conditions are varied to favour the selective removal of H$_2$S while leaving the CO$_2$ as much as possible in the vapour phase; (ii) the vapour exiting the column is sent to a TurboCapture unit; (iii) the CO$_2$ cleaning from the gas at TurboCapture outlet is finalized in a second absorber by means of cold methanol. The main advantage reported by this concept compared to modified-Rectisol is the decrease of solvent circulation rate, hence leading to a lower specific energy penalty for CO$_2$ capture.

5. Pareto optimization of CCS options

The optimization problem has been solved with a black-box approach. Each black-box function evaluation entails: (i) process simulation with Aspen Plus; (ii) solution of the heat integration problem; (iii) evaluation of the objective functions; (iv) computation of CAPEX of the CCS unit. The black-box function is highly non-linear, discontinuous and not defined in some points. As a result, the feasible region is small and non-connected. Moreover, each evaluation requires a relevant computational time (5÷30 s). For these reasons a two-steps optimization framework has been implemented, by adopting parallel computing on a 12 core workstation: the 1st multi-objective optimization step explores effectively the solution space with a derivative-free algorithm; the 2nd single-objective optimization passage performs a "Push-Pareto" step to improve the non-dominated solutions generated after step 1.

6. Optimization results and conclusions

The applied optimization methodology, which has proved to be feasible and potentially attractive and implementable also at the industrial level, made available designs of the CCS island which look promising when compared with the reference ones.
As a matter of fact, the hybrid process, designed and optimized for a 90% capture in an IGCC, is capable of lowering the specific electric equivalent consumption of the capture section by 20% when compared to a conventional Selexol scheme. Moreover, the flowsheet improvements proposed in the modified-Rectisol, when compared to a conventional Rectisol, introduce a significant reduction of the energy penalty of the capture process, in some configurations (very high capture rates in a CTL plant) reaching a decrease of 30%.
The patented TurboCapture process looks very attractive for application requiring medium-low CO$_2$ removal rates, namely below 85%.
Finally, the overall detailed thermodynamic assessment of an IGCC plant, conducted for CO$_2$ capture rates ranging between 60% and 99%, reports an energy penalty varying between 5.8 and 7.5 percentage points compared to the no-capture scheme, resulting in an efficiency improvement of the order of 1-2 percentage points with respect to the state-of-the art pre-combustion technologies.

TRANSIENT EFFECTS IN LINEAR CONCENTRATING SOLAR THERMAL POWER PLANT

Andrea Giostri - Supervisor: **Ennio Macchi**

Introduction

The main object of the PhD work can be identified in the analysis of transient effects in Linear Concentrating solar thermal power plant (CSP) (Heat Transfer Fluid based -"HTF"). The thesis work outlines can be summarized in three different parts. The first is the study of the annual energetic evaluation of a linear CSP plant with the quasi-steady state approach that represents the most common simulation approach. The topic of the second part is the analysis of some aspects related to transient behavior of the solar field (SF) during specific situations as, for example, the mass flow rate distribution with cloud shading some part of SF or the thermal behavior during the morning warm-up. The subject of the last part is the comparison of annual energy output between a quasi-steady approach and an approach that considers some aspect related to transient effect in order to identify the difference in annual energy yield prediction.
As regards the international collaboration established, a part of the PhD activity was carried out at Solar Research Group of the German Aerospace Center (DLR) located in Stuttgart.

Steady state

The first part of the PhD thesis work focuses on quasi-steady state analysis of CSP plant. This procedure represents the most common approach to establish the yearly performance of the whole plant. In particular, the CSP modelisation can be divided in two steps; the first is the sizing of both the solar field and the power block section and the second is the prediction of part-load performance. The quasi-steady state approach refers to the part-load performance prediction; this methodology consists of considering the plant operation as a succession of steady states without the addition of any transient effects. Operatively, each time step depends on the instantaneous weather conditions without considering the previous time steps. The detailed description of this approach is presented with the help of two exemplificative studies that deal with the comparison of different technology solution for parabolic trough technology and the comparison between the parabolic trough and the linear Fresnel technology respectively. To accomplish the annual energy yield calculation both an in-house code, called PATTO (parabolic trough thermodynamic optimization), and a commercial code (Thermoflex®) are used.

Piping model

In order to correctly calculate the transient behavior of the solar field, a detailed model of the piping system has to be implemented. In particular, the physical dimension of each pipe segments (e.g. mass of steel, mass of HTF contained) and the expansion vessel influence the thermal inertia of the solar field that plays a fundamental role in the transient behavior of the whole system.
A specific MATLAB suite was developed with the purpose of sizing the piping network; in particular the sizing is combined with an optimization procedure with the aim of determining the optimal configuration in terms of minimal total cost (sum of investment and operational cost). For this purpose a cost-database of piping system components is obtained from a literature review. As input the algorithm requires the nominal HTF mass flow, the physical dimensions of the solar field and the characteristics of the available pipe. The code outputs are represented by the outer commercial diameters, the wall thickness, the thickness of the insulating material for each pipe segment and the dimension of the HTF thermal expansion system.

Dynamic Thermal model

To study the transient SF behavior a specific algorithm was coded in MATLAB; in particular this code implements the characteristic equations to solve the thermal behavior of the absorber tube able to capture the main transient effects. In particular, the time dependent contributions are added to the steady-state formulation proposed by Forristall. Taking into account that a SF is commonly composed by many loops connected each other by the piping system, the single absorber model represents the elemental unit of the thermal model. In addition, the hydraulic network modelling is necessary to compute the mass flow distribution in the solar field. As regards the power block modelisation, due to its lower (approximately 1:5) thermal inertia compared to the solar field one, a polynomial approach is considered in order to obtain a good compromise between the accuracy and the computational efforts.
A test-case cloud disturb, considered as an obscuring square that moves with an arbitrary trajectory, is selected in order to identify the solar field response during the passage of the cloud. In particular the solar field response is evaluated considering the mass flow distribution, the outlet temperature from both each loop and the expansion tank temperature that represents the temperature of the HTF stream entering in the power block. Following the real plant approach that in the most of cases considers the total HTF mass flow as the only control parameter of the solar field, some simple HTF total mass flow control strategies are compared in order to detect the best one from an energetic point of view.

The obtained results suggest to maintain a constant HTF mass flow rate during the passage of a cloud; the most important advantages of this strategy can be summarized in the high level of simplicity, the absence of a control valve on each loops and the minimization of the defocused energy without reaching a HTF temperature level inadequate for power block operation. It is important to underline that the general results could be slightly influenced by different boundary conditions related to the cloud disturb.
In addition, the model is used to study the solar field behavior during the morning warm-up; in particular, the solar field is operated in recirculation mode and the non-uniform reciprocal shading of parabolic trough causes a different behavior among shaded and non-shaded loops (the most eastward during the morning). The results obtained shows that no unsecure situations occur, underlying that during the morning warm-up a safe operation is possible without applying complex control strategy or defocussing a part of the solar field.

Cloud vector

In order to increase the accuracy level of the modelisation, the cloud disturb is analyzed in detail. Using solar radiation data from ground measurement installed in Spain, the Cloud Movement Vector (CMV) is computed by a specific procedure proposed by Bosch and written down in MATLAB language. As regards the cloud transmissivity factor, the experimental measurement grid is used in order to develop a discretized opacity map. The cloud info obtained are set as an input in the CSP plant model in order to evaluate the effect of a more detailed description of the disturb. As a qualitative conclusions, the addition of the opacity distribution has a negligible effect on the thermal performance of the solar field; in particular the substitution of the opacity map with an uniform opacity value, equal to the spatial mean value, leads approximately to the same results diminishing at the same time the computational resources needed.
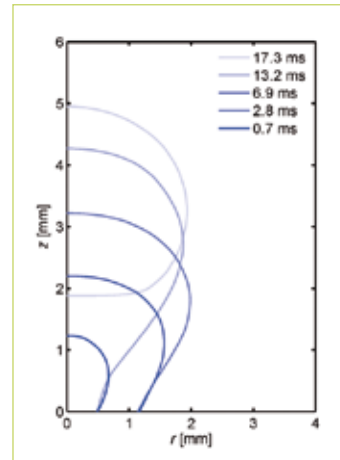
Conclusions

After the study of some typical transient effects of solar field, a comparison about the yearly energetic yield prediction was performed considering both a quasi-steady state methodology and a model that considers the SF thermal inertia.
Different increasing time periods are simulated (i.e. days, weeks and year) in order to have a complete idea of the differences between the two models. The found results are in agreement with independent studies found in literature that report an annual energy output overestimation of ca.10% by the quasi-steady state approach. This result confirm the necessity to consider the transient effects in annual energy yield using specific model or correcting the quasi-steady results with specific parameters.

TWO-PHASE HEAT AND MASS TRANSFER MODELING: FLEXIBLE NUMERICAL METHODS FOR ENERGY ENGINEERING ANALYSES

Gaël Guédon - Supervisor: **Fabio Inzoli, Emanuela Colombo**

Developing a high resolution numerical method for the simulation of two-phase heat and mass transfer is a viable way of getting deeper insights into such phenomena, and as consequence to better understand them. Two-phase heat and mass transfer phenomena play an important role in several natural processes and engineering systems. Knowledge about the mechanisms governing such phenomena is therefore of interest for the understanding of our environment and for the design of safe and efficient technical components. As a consequence, researchers and engineers have continuously performed experiments and developed mathematical models for the description of such phenomena. In spite of all their efforts, many of the physical phenomena that occur during two-phase heat and mass transfer and their interaction are still not well understood. Accordingly, current efforts are directed towards higher resolution experiments and numerical models in order to provide better understanding of two-phase heat and mass transfer processes. In the recent years, the spatial and temporal resolutions of the experiments have continuously increased while few high resolution mechanistic predictive tools, to be used in parallel to

the experiments, have been developed. The development of reliable and flexible high resolution numerical models is thus an active field of research nowadays.

This work is a contribution to this common goal by suggesting a numerical framework for the simulation of phase change phenomena. Due to the wide field of applications making use of two-phase heat and mass transfer, the proposed phase change model is focused on boiling phenomena, which is a relevant mode of heat transfer in the energy sector. However, the developed model may be easily extended to other types of heat and mass transfer phenomena, such as condensation, thanks to the flexibility of the code used. Boiling is a very efficient mode of heat transfer and plays a major role in several engineering systems for the production and conversion of energy. Despite its wide use, the design of heat exchangers still relies on empirical correlations that have been developed during the second half of the twentieth century, because the numerical methods for the simulation of boiling phenomena are still not well established. The several spatial scales involved in boiling phenomena constitute one of the main difficulties in the development of a reliable numerical method. Various numerical issues also arise due to

the presence of moving two-phase interfaces. The correct prediction of capillary forces, mass transfer rate and heat transfer, with an optimized computational cost, is the principal challenge of nowadays numerical models.

The proposed numerical framework is developed using the open-source OpenFOAM Computational Fluid Dynamics toolkit, which permits a high flexibility and sustainability of the model. The Finite Volume discretization method is used to solve the governing equations of the problem. The method is compatible with general unstructured meshes in two- and three-dimension.

1. Velocity vector field around a spherical rising bubble of diameter 0.9 mm. Four different interfacial curvature calculation methods are analyzed.

A mass-conservative Volume-Of-Fluid interface tracking method is adopted to capture the position of the two-phase interface and its influence on the fluids flow. Four interfacial curvature calculation methods for the prediction of surface tension are implemented and compared: namely the *Gauss, node-based gradient (nbg), recursive weighted interpolations (rwi) and height function (hf)* methods. The mass transfer rate is computed directly from the heat flux at the interface using a reconstructed Level-Set function from the 0.5-isocontour of volume fraction. The sources due to mass transfer are then concentrated near the interface. Adaptive mesh refinement is possible in three-dimension and the mesh is usually refined near the interface, where a higher mesh resolution is beneficial for the correct prediction of the mass transfer rate.

The detailed description of the governing equations and of the implemented numerical model is followed by a verification and validation process. Dedicated test cases are employed for the isothermal and phase change part of the model. Isothermal static bubbles and capillary waves are studied to evaluate the accuracy of the implemented interfacial curvature calculation methods. The proper implementation and validation of the phase change model is
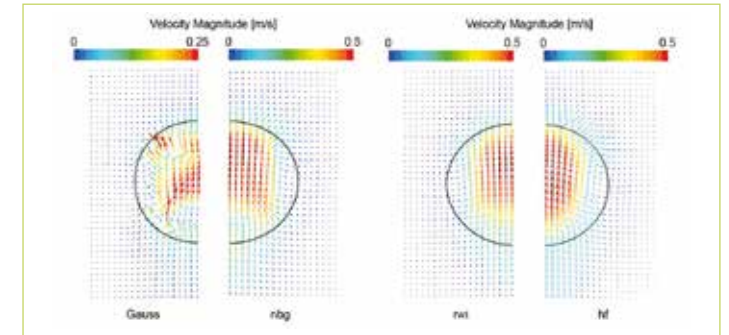
2. Bubble interface shape evolution during nucleation, digitized from experimental data.

then performed by investigating the Stefan, sucking interface, and spherical bubble growth problems. The several numerical issues related to two-phase heat and mass transfer are identified and the accuracy of the model is assessed.

The present thesis also contains a detailed study of isothermal spherical rising air bubbles in water with dimensions typical of heat and mass transfer applications. A thorough review of the experimental and theoretical works is performed in order to identify the most appropriate reference data for the comparison with the numerical model. A high dependence of the bubbles' terminal rising velocity on the interfacial curvature calculation method is observed, suggesting the use of the *hf* method implemented in the open-source

Gerris Flow Solver code. In Figure 1, a comparison of the four interfacial curvature calculation methods for the simulation of a spherical rising bubble is given in terms of velocity vector distribution and interface shape. A net reduction of the unphysical velocities near the interface is observed for the *nbg*, *rwi* and *hf* methods.

Finally, a benchmark for the simulation of nucleate boiling is developed using experimental data from the pool boiling facility of the Department of Nuclear Science and Engineering of the Massachusetts Institute of Technology. The evolution of the bubble interface shape during nucleation is digitized (see Figure 2) and the temperature field at the heater surface has been post-processed for direct comparison with future numerical results.

A STUDY OF ALTERNATIVE DESICCANT COOLING MATERIALS AND EQUIPMENT FOR LOW TEMPERATURE TRIGENERATION SYSTEMS

Manuel Intini - Supervisor: Prof. Ing. Cesare Maria Joppolo

The aim of the present work is to investigate on potential improvements for desiccant cooling air conditioning units coupled with low temperature fuel cell-based trigeneration systems. Fuel cell technology is an extremely promising solution for small scale combined heat, cooling and power (CHCP) production owing to their potentially high efficiency, low noise and near-zero emissions. In the vast scenario of fuel cells, polymer electrolyte membrane ones (PEFC) are proved to be the most mature and almost close to the commercialization; however, owing to its very low operating temperatures (below 80°C), coupling PEFC with a thermally driven cooling process might be extremely demanding. With such crucial constraints on regeneration temperature there exist two main fields in which desiccant cooling performance can be improved. The former is a desiccant driven approach, in which alternative desiccant materials with more favorable isotherm shape are investigated. The latter consists in finding out optimal system configuration in order to minimize primary energy consumption.

It is broadly known that regular density silica gel is quite a well performing adsorption material whose main drawback consists in its almost linear adsorption isotherm, with no rapid variation in moisture uptake as a function of equilibrium air relative humidity. Among alternative desiccant materials, zeolite based-molecular sieves show a typical S-shape adsorption isotherm which is ideally good for dehumidification and drying process. Yet adsorption isotherm steepest gradient zone is in the very low humidity range, i.e., the minimal amount of adsorbed water vapor is achieved only at extremely low relative humidity; this means, in turn, very high regeneration temperatures. New generations of synthetic zeolites recently referred to as FAM (Functional Advanced Material) benefit from a particular adsorption isotherm steepest gradient zone that is significantly shifted towards higher relative humidity values; therefore, dehumidification can be even better than the one attained with conventional materials in the same working condition range.

First, a comprehensive experimental campaign has been carried out in two test facilities: the compact climate test facility at CSIRO Energy Centre (Newcastle, Australia) and the advanced desiccant wheel laboratory at Politecnico di Milano. As a considerable part of the whole project, test facility design description is provided and experimental procedure broadly discussed.

Experimental campaign has involved mainly two different desiccant wheels based on silica gel and advanced zeolite respectively. Tests have been accomplished as a function of air inlet humidity for different level of regeneration temperatures, with constant area split and adjustable revolution speed. Dehumidification performance proved to be significantly dependent on inlet water vapor mass fraction and moisture removal capacity appeared to increase with inlet humidity. However, zeolite-based desiccant wheels show less than a linear trend, while silica gel-based wheels keep good water vapor removal rate even for very high humidity. This discrepancy has been justified with zeolite peculiar isotherm curve, which achieves maximum water uptake for equilibrium air relative humidity higher than 60%. A finite difference time dependent numerical model has been developed as a tool to predict and optimize desiccant wheel performance in air conditioning systems. A gas-solid side numerical model has been chosen in order to take into account the effect of both air side and desiccant side internal resistances. Model has been validated on experimental data and good agreement is achieved for low and medium regeneration temperatures.

Optimization analysis show that maximum latent cooling capacity is always attained with equal cross section split for both desiccant, as long as regeneration temperature is lower than 80°C. Only for high temperatures maximum latent cooling capacity is achieved with a wider process cross section fraction, close to 0.6. Therefore, if low grade heat is considered as thermal driving force, area ratio must be set close to 0.5. As a result of comparative analysis, FAM dehumidification performance is quite similar for low process flow water vapor mass fraction (RH<40%), despite a larger differential moisture uptake in the moderately high relative humidity range. For dump conditions a regular density Silica Gel desiccant wheel performs better, especially in the low regeneration temperature range (50-60°C), up to 15% more in terms of moisture removed. For higher grade heat, moisture removal discrepancy between the two desiccant devices decreases and reverses owing to a better dehydration of molecular sieves desiccant layer. In the range of substantially similar latent cooling capacity zeolite desiccant leads to higher rise in process temperature and the aforementioned temperature glide increases with regeneration temperature. It is found that for low regeneration temperature applications and very humid process air streams novel zeolite desiccant wheels are not appropriate to perform desiccant cooling based air conditioning, while in mild climate desiccants can be considered almost equivalent.

The final section of the work focuses on overall system design and seasonal performance. Since low grade heat-driven single stage desiccant cooling is barely sufficient to cool down fresh air stream properly, double stage desiccant dehumidification and coupling with backup conventional cooling devices are investigated. Hourly energy simulations are set on a reference case based on open loop air conditioning system with high level of occupancy. Simulations include detailed models of adsorption devices and semi-empirical correlations fit on experimental data for heat and mass recovery exchangers. It is found that secondary stage dehumidification involves relatively warm and dry process air streams, therefore with double stage applications FAM Zeolite wheels can achieve greater latent cooling capacity with better heat recovery and, in turn, higher thermal coefficient of performance. The higher the temperature at which the desiccant swing occurs, the greater the efficiency zeolite based systems lead to. On the other hand, integration of chilled water cooling coils does require high relative humidity targeted desiccants, therefore regular density silica gel still remain the best available solution. In addition, hybrid cycles prove to be less sensitive to outdoor conditions, while double stage cycles show lack of flexibility for off-design control.

The aforementioned alternative desiccant cooling systems are compared with conventional vapor compression chiller technology over the entire cooling season. It is found that silica gel-based desiccant cooling solution can achieve primary energy saving up to 10% even with baseline electrical power efficiency (22%) and for advanced technology scenario this value may be almost doubled. Maximum regeneration temperature can be kept at 60°C and no indirect evaporative cooling is needed on secondary air stream. Given the same operating conditions, double stage desiccant cooling cycles provide a lower cooling capacity than expected, with a larger amount of regeneration heat and higher ventilation consumptions. This implies that achieving primary energy saving is crucial with baseline CHP systems. For advanced scenarios, if CHP electrical efficiency can be raised up to 30% double stage desiccant cooling might be an alternative solution to hybrid cycles. For very low grade heat, it is found that advanced zeolite-based desiccant cooling may attain poor effective benefit. Only if regeneration temperature can be raised up to 70°C an effective advantage over conventional cycles may be achieved.

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

LARGE EDDY SIMULATION FOR COMPLEX INDUSTRIAL FLOWS

Paolo Lampitella - Supervisors: **Prof. Emanuela Colombo**

The object of this thesis is the Large Eddy Simulation (LES) of turbulent flows, its theoretical and practical development toward complex industrial flows requiring unstructured flow solvers and its specific application to flows of different complexities.

In a broad sense, LES deals with approximations of the dynamical system described by the Navier-Stokes equations (NSE), the approximation being in the use of a lower number of degrees of freedom (i.e., the number of grid cells and time steps used in a computation) than those strictly required for a correct full numerical simulation of the flow (i.e., DNS). In LES literature, the reduction in the number of degrees of freedom is usually introduced by formally applying a spatial low-pass convolution filter to the NSE. This filter is aimed at separating the large turbulent scales, which in LES are directly represented on a grid and simulated, from the small or sub-grid scales (SGS), which in LES are only modeled, i.e., by a SGS model. The rational basis for this approach and, as a matter of fact, for LES as a whole, stems from the classical Kolmogorov picture of the turbulent energy cascade. The large scales are the most energetic, anisotropic and the most dependent from the boundary conditions. Small

scales, in contrast, are much less energetic, more isotropic and universal, hence they should be relatively easy to be modeled. However, nowadays, it is fully recognized that the actual dynamical system effectively represented by the numerical simulation is different from the formally filtered NSE in several aspects. First and foremost, the effective scale separation between resolved and modeled scales is usually different from the theoretical one which, in most cases, is not even present in practice. As a consequence, the overall scale separation is actually determined by the computational grid, the numerical scheme and, possibly, the SGS model too. This, in turn, introduces uncertainty in the computation as both the resolved and the modeled scales are not precisely characterized and the SGS models, which are developed in such incorrect framework, are also required to represent a not well specified range of scales. A second important aspect concerns the specific form of the equations used for the simulation which, despite the issues described above, is still usually based on the formally filtered NSE. This approach either introduces additional modeling errors, known as commutation errors, or requires specific numerical strategies and numerical

methods with higher accuracy. These problems, which might appear secondary or abstract, are in fact fundamental. Indeed, the overall LES approach can be essentially reduced to the interaction between a scarcely resolved, numerically affected, range of scales near the cut-off of the grid, and a SGS model, which should represent the interactions of such scales with the missing ones. Whenever this interaction is misrepresented, the outcome of the simulation is strongly affected. Moreover, this picture is even more critical when considered in the framework of unstructured flow solvers, usually adopted in practical engineering applications. Indeed, the hypotheses required to fit the formal LES picture are seldom, if ever, satisfied and the higher numerical accuracy required to overcome this limit is not usually available or practical. Despite its high resolution requirements, LES is now feasible for small-medium sized industrial applications and is explicitly required whenever the flow presents strong unsteadiness or interactions among different spatial scales. As a consequence, in order to further develop LES for complex industrial applications, it is of paramount importance to overcome its present deficiencies and limitations. In the present

work, this objective is pursued by first reformulating the LES problem in a new, consistent, theoretical framework. In particular, the classical LES route described above, in which model filtered equations are used as representative of a numerical approach, is definitely abandoned. Instead, the new proposed framework is defined by equations which are an exact representation of a given numerical method, independently from any filter concept. In particular, this framework is more general than the classical one as it exactly represents most of the known numerical approaches: finite differences, finite/spectral element methods and finite volumes (FV), structured and unstructured. As such, it is particularly suitable as theoretical framework for the development of LES in complex applications using unstructured flow solvers of any type. Moreover, as a side-product of the present LES reformulation, relevant differences arise at the level of the SGS terms which need modeling and their underlying algebraic relations, also known as Germano Identities. These differences are such that important reductions in the computational costs of some classical SGS models are introduced and more complex modeling options can be

explored with relative ease. This last aspect, in particular, is further developed in the thesis trough the application of the proposed framework to the FV method. As a result of this application, a new SGS model is developed, which is intended to recover part of the energy lost by the numerically affected scales of the flow, while remaining stable on general unstructured grids. The flexibility and suitability of the proposed LES approach and SGS model are then demonstrated by their implementation in a general purpose unstructured FV solver and the application to flows of increasing complexity. A particular attention is first devoted to the turbulent channel flow, because of its relevance as LES benchmark and the availability of solutions with different codes and SGS models. More specifically, the comparison is made with the codes participating the LESinItaly database, ranging from pseudo-spectral to finite difference ones, including several commercial and open-source FV codes. The comparison not only shows the relevance of the proposed SGS modeling strategy, which outperform all the reference LES solutions, but also evidences a striking similarity of LES results among very different codes. This similarity is further investigated

and possible causes are highlighted, leading to a better interpretation of common results found in literature. Finally, more complex flows are considered. These include: turbulent pipe flows computed with unstructured grids at different Reynolds numbers; the flow and heat transfer in a matrix of wall-mounted cubes; the cold, swirling, flow in a lab-scale industrial combustor. In all the cases, the proposed SGS model is compared with the available DNS/experimental data and with more classical SGS modeling strategies using multiple grid resolutions. The results of these additional tests show that the proposed SGS model is, at worst, as accurate as the classical SGS models, while retaining its stability and lower computational costs. However, for the lower resolutions typical of industrial applications, the effects of the new SGS model are more evident and lead to a better prediction of the flow statistics.

A NOVEL DETECTION SYSTEM FOR DIRECT AND HIGH RESOLUTION SPECTROMETRY OF INTENSE NEUTRON FIELDS

Michele Lorenzoli - Supervisor: **Prof. Stefano Agosteo**

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

The aim of this PhD thesis was to develop an innovative detection system capable of measuring spectral fluence distributions of intense neutron fields with high resolution.

The basic idea is to use as a converter a plastic scintillator able to measure the energy released in the converter itself by recoil-protons generated by impinging neutrons. A Monolithic Silicon Telescope (ΔE stage and E stage), measuring the residual proton energy, is placed at a proper distance from the scintillator in order to limit the detection to protons emitted at small angles. Event-by-event, the sum of the energy deposited at each stage gives the total energy of the recoil-proton, therefore the energy of the impinging neutron (since the emission angle is fixed).

The requirement of positioning the scintillator far away from the silicon telescope leads to install the detection system in vacuum in order to minimize the attenuation of recoil-protons. This Active Converter Spectrometer (ACSpect) is conceived for a direct real-time collection of neutron spectra, without the need of unfolding procedures.

A detailed study was also carried out in order to investigate the optimum coupling scintillator-photomultiplier. This work
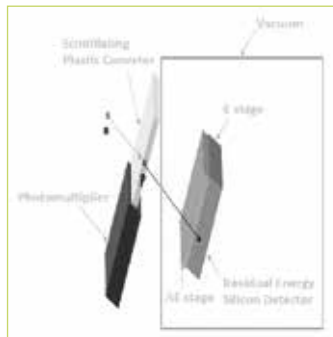
1. Concept of the ACSpect.

was based on the analysis of performances of commercial Photomultiplier Tube (PMT) and a Silicon Photomultiplier (SiPM). Despite the advantages in the dimensions and in the working conditions (no high voltage required), the SiPM shows a worse resolution. After preliminary tests with neutrons, the SiPM devices resulted to suffer from an high radiation damage, therefore unsuited for working in fast neutron fields. The complete system was irradiated with monoenergetic neutrons at different energies at the INFN-LNL facility. The time coincidence and selection between the three stages events (ΔE stage, E_{TOT} stage, scintillator-PMT) were performed by exploiting the ΔE-E_{TOT} structure of the MST. The ΔE-E_{TOT} events are firstly collected with a simple time coincidence procedure. The

recoil-protons are then easily discriminated from other kind of events by processing the ΔE-E_{TOT} distribution.

Without this proton selection the time occurrence distribution of the photomultiplier events in correspondence of the ΔE events presents a large number of false coincidences, mainly due to the strong γ background; by applying this selection and by performing a time-energy coincidence the correct distribution can be identified. The converter proved to have a non-linear behavior; this is due to a non-linear dependence of the specific scintillation light on the stopping power of recoil-protons dE/dx, well described by the Birks' law.

In order to reproduce the experimental results, an analytical model based on the Birks' law was developed; this model computes the light emitted by a proton with energy E_p stopping in plastic. A correction procedure was implemented; it calculates the equivalent quantity of light L_{EQ} that corresponds to the residual recoil-proton energy measured by the telescope E_{TEL}. The quantity L_{EQ} is then summed to L_{SCINT} to estimate the total light (L_p) generated by a recoil-proton of energy E_p. Finally, the total recoil proton energy E_p is derived from L_p by applying the reverse model.

The system was characterized with monoenergetic neutrons (protons on LiF) at different energies. This allowed to assess an energy resolution of 235 keV FWHM (Fig.2, left). This measurements were performed with a detection efficiency of ~10^{-6} counts per neutron. The ACSpect was irradiated with continuously distributed neutrons.

The continuous neutron spectra generated by protons on a thick Be target were compared with time-of-flight data. This comparison (Fig.2, right) shows a good agreement between the spectra.

The continuous neutron spectra generated by deuterons on a thick Be target were compared with data simulated without taking into account the reaction channels occurrence. This comparison shows a good agreement between the peak energies.

The aim of this research activity was to develop an innovative detection system capable of perform real-time neutron spectra measurements with high resolution. An innovative procedure for events discrimination was developed, exploiting the MST structure and the time-energy correlation between the
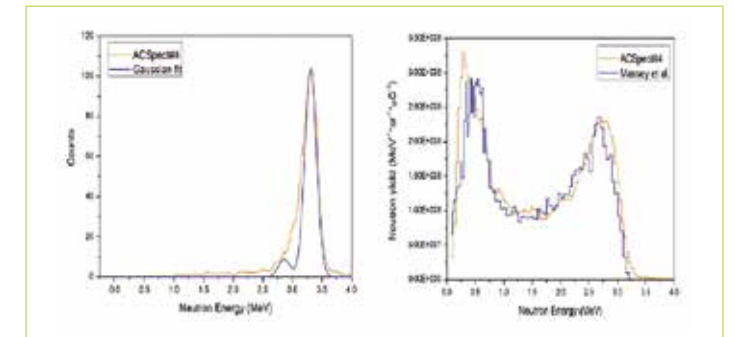
2. Spectra of neutrons generated by 5 MeV protons on LiF (left) and Be (right) targets.

three stages, leading to a very accurate proton selection.

An innovative procedure was developed to manage the non-linear behavior of the plastic scintillator; by combining the information measured by the PMT and E_{TOT}, it easily calculates the total energy of the recoil-proton.

These two procedures together with the optimized layout of the system are the key of the achieved results of the ACSpect. The system proved its linear behavior and a FWHM of 235 keV; it has to be noticed that the beam provided by LNL is not characterized, so its uncertainty could affect the width value. A three-stages neutron spectrometer, operating in vacuum, was proposed in 2010 by Tomita et Al.; this system proved to obtain a resolution of ~200 keV and a detection efficiency of 10^{-7}-10^{-6}; to obtain

this results, the system needs a very thin plastic converter (100 µm) and a large overall system, compared to the ACSpect (2 mm of converter, 122x173x51 mm).

This comparison proves the ACSpect as a good candidate system for the development in its research field.

TURBOMACHINERY DESIGN OPTIMIZATION BASED ON USING ADJOINT METHOD AND ACCURATE EQUATIONS OF STATE

Matteo Pini - Supervisor: **Prof. Vincenzo Dossena**

This thesis concerned the development of a shape optimization approach for turbomachinery applications based on a gradient-based adjoint method coupled to complex equations of state for accurately dealing with fluids exhibiting relevant real gas effects.

The design algorithm proposed has been equipped with a discrete inviscid adjoint method able to treat real-gas flows, state-of-the-art parametrization techniques (NURBS) and a preconditioned steepest descent optimizer to search for the optimal point. The mathematical approach followed may be regarded as an extension of the seminal adjoint theory to include a generalized thermodynamic treatment. Therefore, built-in equations of state (e.g. Van der Waals) and a look-up table (LuT) approach have been introduced within the optimization algorithm, both at flow and adjoint solver level, to handle real-gas effects. In particular, the novel consistent LuT method has been devised to fully exploit the capability of external thermodynamic libraries (e.g. RefProp, StanMix).

The potential of the optimization approach has been investigated on different 2D design problems typically encountering in aerodynamics and turbomachinery. The design methodology has been initially applied to the re-design of a wind tunnel nozzle operating under both ideal and real gas flow conditions.

Then, two different turbomachinery design applications have been faced. The former regarded the maximization of the performances of a transonic cascade and represented the earliest test case carried out in this research. The latter aimed at optimizing an existing supersonic turbine cascade with the objective of achieving a more uniform flow at blade outlet section in reference conditions. The baseline and the optimized blade are reported in Figure 1. Real-gas flows of siloxane MDM have been considered in this latter application.

An original extension of the algorithm for treating off-design conditions has been also conceived in the research. The method combined the favourable features of a standard multi-point optimization technique with the advantages provided by the stochastic collocation uncertainty quantification algorithm to assess the design points and the weights of the multi-point problem. The capability of the novel approach in providing robust designs has been finally tested by maximizing the performances of the previous mentioned supersonic blade, now working under a relatively wide range of operating conditions. Results showed a considerable attenuation of the fluctuations of the performances while changing the static backpressure, which has been identified to be the parameter mostly affecting the turbine performance.

In all test cases remarkable outcomes have been achieved in terms of improvement of performances of the initial configuration with very limited computational expenses. This makes the adjoint method very attractive compared to more demanding evolutionary algorithms, especially whereby the re-design of existing configurations is of primary interest.

Most of the applications of adjoint method are still restricted to shape optimization, however new perspectives have been recently risen around the use of adjoint. In this respect, the final part of the research has been devoted to investigate the potential of adjoint-based methods for uncertainty quantification and robust optimization. A simple quasi 1-D nozzle problem has been taken as reference for the thorough analysis. Results proved the capacity of adjoint-based UQ methods (e.g. Method of Moments) for rough but very cheap estimate of first and second statistical moments (mean and variance) of cost functionals (e.g. nozzle efficiency) compared to non-intrusive approaches (polynomial chaos). These moments, although quite inaccurate when shock-dominated flows are considered, have been be successfully used as objectives to minimize through robust optimization algorithms, in order to achieve nozzle designs less sensitive to aleatory variations of the input parameters.
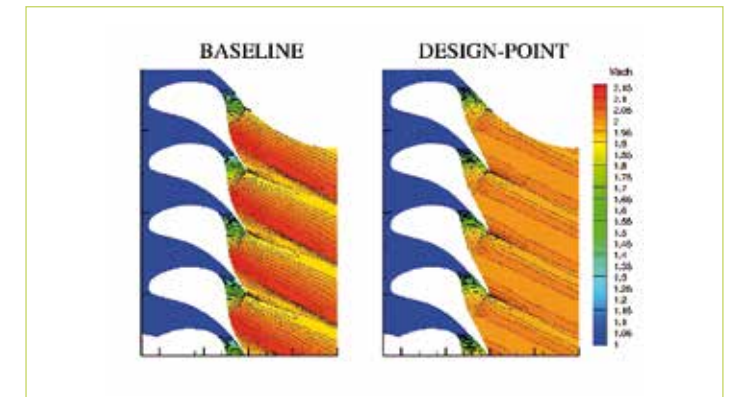
1. Baseline and optimized blade (left frame) and isentropic Mach number distribution along the blade surfaces (right frame). Notice the more uniform flow in the optimized configuration, resulting in a decrease of the fluid velocity along the rear suction side.
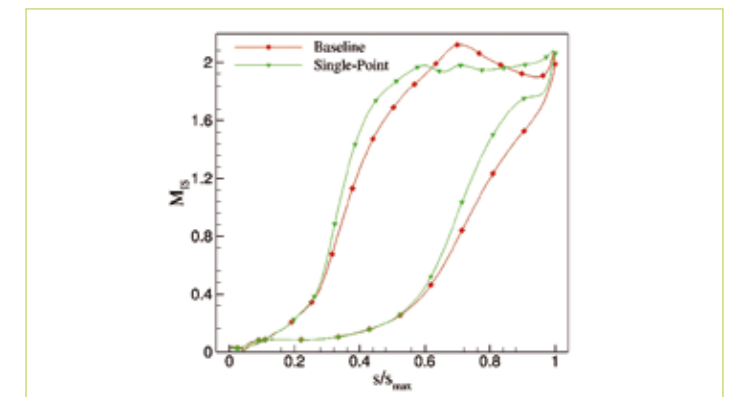

2.

DEVELOPMENT OF A MODEL-BASED APPROACH FOR STUDYING THE SYSTEM DYNAMICS AND CONTROL OF GEN IV LEAD-COOLED FAST REACTORS

Roberto Ponciroli - Supervisor: **Prof. Antonio Cammi**

The Lead-cooled Fast Reactor is one of the six innovative systems envisaged by the Generation IV International Forum in order to provide sustainable, safe and proliferation resistant nuclear energy production. The LFR system has excellent materials management capabilities since it operates in the fast-neutron spectrum, and uses a closed fuel cycle for efficient conversion of fertile uranium. It can also be adopted as incinerator to consume actinides from spent Light Water Reactor fuel or as *adiabatic reactor* (able to burn the self-generated actinide waste). This reactor concept offers a great potential for plant simplifications and higher operating efficiencies, introducing at the same time safety concerns, design challenges, and technological constraints brought by the use of lead as coolant, different from both water-cooled reactors and other fast systems. In particular, this reactor has some peculiarities, such as a large thermal inertia and a very corrosive coolant environment, that determine strict constraints on the temperature field. Such different operating conditions increase the need for enhanced I&C capabilities. At the present time, dedicated analyses regarding the control strategies for this reactor concept are not available in literature, and

the LWR procedures cannot be directly employed. In this sense, the subject of the thesis work is the development of an integrated methodological approach for the study of dynamics and the definition of control strategies for LFRs, adopting ALFRED (Advanced Lead Fast Reactor Demonstrator) as a reference reactor configuration.
As a first step, the stability features of the overall system have been characterized. The knowledge of the system dynamics is of primary importance for the study of plant global performance and for transient design-basis analysis since it accounts for the interactions among input and output variables, while providing useful guidelines for the design of a suitable control system. Indeed, since it has not been possible to rely on any operational experience, a model-based approach has been adopted, and dedicated quantitative techniques, which allow conceiving the most efficient control strategy starting from the constitutive equations, have been employed. Therefore, the root locus method has been adopted so as to demonstrate that no problems arise in plant operation at reduced load factors as well. In this way, the system stability through the calculation of the

system eigenvalues and the corresponding trajectories in the Gauss plane has been assessed. In addition, such a sensitivity analysis has allowed evaluating how the stability features are affected by the coolant density reactivity coefficient, providing useful feedbacks to the system design finalization.
In order to properly characterize the ALFRED governing dynamics, it has been necessary to develop an accurate and fast-running simulator representing the entire power plant, and integrable with the control system model. Recent advances in object-oriented modelling, and in particular the development of the Modelica language, constitute a viable path to fulfil such requirements. Therefore, an a-causal, object-oriented and one-dimensional model has been developed, specifically meant to (i) characterize the system governing dynamics, (ii) define the full power control mode with simulation of ALFRED controlled operational transients, (iii) validate the proposed control strategy. In particular, the simulation of design-basis transient scenarios has allowed focusing the structural bonds among input and output variables.
These preliminary investigations have been sustained by the Relative Gain Array, i.e., a quantitative algorithm which
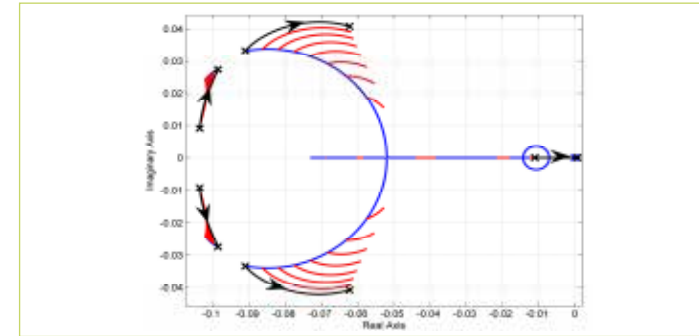

1. Root locus derived for the model of the primary circuit as a function of the power level, accounting for lead temperature reactivity coefficient which varies between 0 and 7 pcm·K⁻¹ at BoC, nominal SG operational conditions.

2. Graphical interface of the developed ALFRED object-oriented model, which has been employed both for characterizing the system governing dynamics and assessing the dedicated control strategies.

allows selecting the most efficient control action for each variable of interest, dealing with an issue that for LFRs has never been studied yet. Once having finalized the control strategy, the scheme based on feedforward-feedback regulators has been implemented.
At this point, after having considered the feasible control strategies, the control system architecture has been finalized. In particular, the reactor start-up procedure has been designed by means of a synchronized Petri net, i.e., a useful tool for the modelling of Discrete Event Systems that allows coordinating the several control actions to be taken during this operational mode. In common practice, the reactor start-up procedure is described by defining the initial conditions of each component of the plant and focusing the sequence of control actions. Conversely, by representing the system desired evolution through this logic-mathematic formalism, it is possible to derive hints for the development of the corresponding control scheme, ensuring the defined controlled evolution. Thanks to this approach, the supervisory

control system that coordinates the operation of the different modulating controllers involved and ensures the switching from the start-up to the full power mode has been developed.
As a last step, the possibility of connecting the ALFRED reactor to the electrical grid so as to perform automatic generation control in reaction to frequency deviations has been studied. Such aspects are particularly important in view of the increasingly relevant fraction of power plants based on Renewable Energy Sources. In the perspective of achieving the plant operational flexibility, it has been tried to adapt the procedure employed in PWRs, namely the *reactor follows*. However, because of the time constants ruling the primary circuit dynamics, it has been necessary to decouple the operation of the primary circuit and the Balance of Plant. In this way, it has been possible to meet the grid demands according to the time constants of the conventional part of the plant so as to fulfil the requirements of the primary frequency regulation.
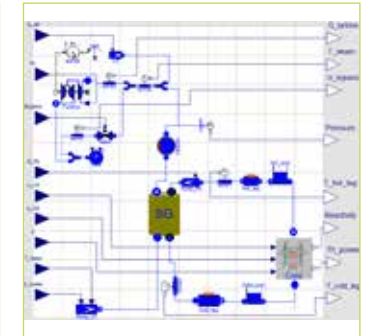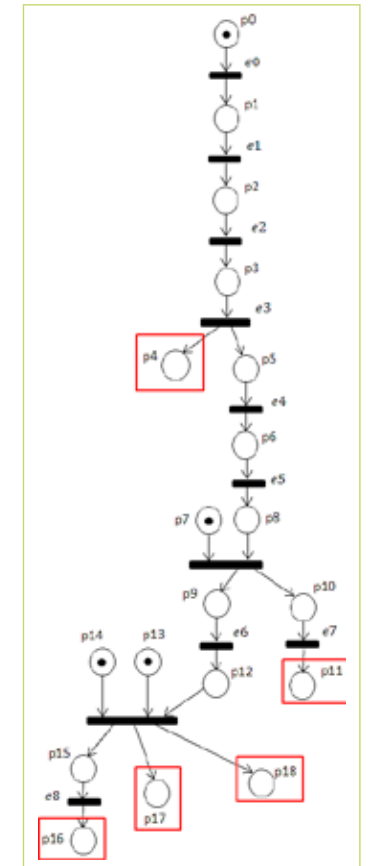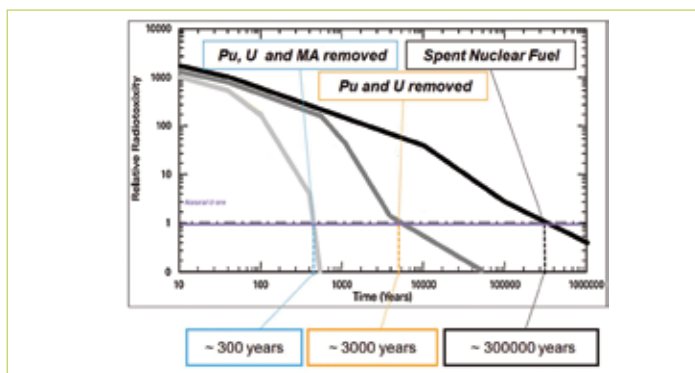

3. Synchronized Petri Net representing the desired behaviour for the ALFRED reactor during the developed start-up sequence. The squared red places are referred to the full power mode conditions.

SELECTIVE SEPARATION OF MINOR ACTINIDES FROM SPENT NUCLEAR FUEL IN HOMOGENEOUS AND HETEROGENEOUS RECYCLING: EXTRACTION PERFORMANCES AND SPECIATION STUDIES OF CHON HYDROPHILIC LIGANDS
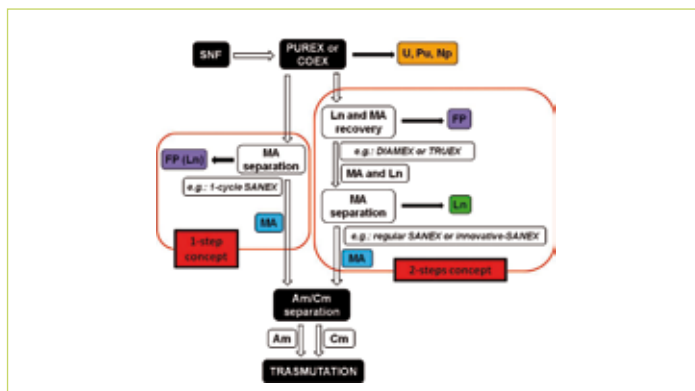
Stefano Scaravaggi - Supervisor: **Prof. Mario Mariani**

In this last years, the scientific community and the power industries are dealing both with the continuous growth of the energetic needs and the diversified energy production: for the social acceptance, one of the fundamental objectives is the substitution of fossil fuels by alternative CO_2 free emission sources. Among them, nuclear energy represents an important contribute to the global energetic supply, but solutions as much environment-friendly as possible (for instance, the respect of CHON criterion) to the new technological challenges, first of all the nuclear waste management, are necessary for its sustainability. If compared to the open cycle strategy, the closing of the fuel cycle and the consequent reduction of the SNF radiotoxicity, allowed by the Partitionig & Trasmutation methods and processes, could result an efficient option and offer significant advantages (see Figure 1).

1. Contribution of Partitioning and Transmutation strategy to the reduction of SNF radiotoxicity

2. Design of the Actinides Partitioning strategies from PUREX raffinate

The rate of decay of SNF components show that the removal of MAs considerably reduces the radiotoxicity of the remaining waste to the level of natural U within some hundreds of years, as opposed to thousands of years. As a consequence, the Actinides/Lanthanides separation step is key issue in the advanced reprocessing, since the low An/Ln ratio and the high effective neutron capture cross sections of Ln elements. This condition inhibits the transmutation of a target containing both Ln and An. Unfortunately, these elements families present a similar chemical behavior, having the same electron configuration in the external shells (4f and 5f, respectively): an efficient solution is to exploit the limited differences in the coordinating properties of a complexing system used in a solvent extraction process. Thus, the selectivity for An over Ln is guaranteed by the different charge/size ionic ratio
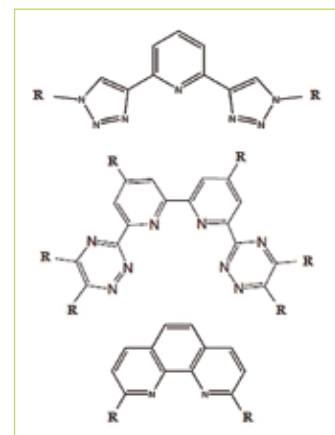
3. Molecular structures of the complexing core of PyTri- (up), BTBP (middle), 1,10-Phen (bottom)

of the metallic cations: the best promising efficiencies were reached by N-heterocyclic tri- or tetradentate compounds (such as BTP, BTBP and 1,10-phen derivatives, presenting pre-organized molecular structures with soft donor atoms faced on the complexing site). Two reprocessing strategies (see Figure 2), aiming at recovering An from the genuine nuclear waste and based on liquid-liquid processes, were proposed and investigated within different international projects supported by Euratom Program. The first approach is based on the direct An removal from SNF (1-step processes, such as 1-cycle SANEX), while the second one resorts to two consecutive steps: first, the An/Ln co-extraction from SNF and then their separation (2-steps processes, such as i-SANEX or GANEX, respectively hetero- and homogeneous recycling).

This PhD thesis was developed as a part of the ACSEPT project (wherein Politecnico di Milano

by means of the Radiochemistry Lab is one of the partners) and two Joint Research Projects (ACTINET I-3 and TALISMAN) between POLIMI and CEA. Its main objective is the assessment of the performances of new hydrophilic complexing agents (see Figure 3) to use in the An/Ln separation step of SNF: these molecules were synthesized in the Radiochemistry Lab (1,10-phen: phenanthroline rings as complexing core) or in the University of Reading (BTBP: the donor set is composed by a central BiPyridine and two lateral Triazine) or in the University of Parma (PyTri-: featured by a central Pyridine and two lateral TRIazol).

A large number of batch tests were carried out in order to verify, by following the i-SANEX (heterogeneous recycling of trivalent Actinides) and GANEX (homogeneous recycling of the Actinides group, that is elements at different oxidation state) protocols, their ability to recover Actinides from a nitric solution simulating the genuine nuclear waste. First, the extraction efficiency and the An/Ln selectivity were evaluated by two main parameters: Distribution ratio ($D = [M]_{org}/[M]_{aq}$) and Separation Factor ($SF_{1/2} = D_1/D_2$). Then, the experimental research was focused on those chemical mechanisms regulating the formation and the stability of the coordination compounds: complexation equilibria and favorable stoichiometries of the complexes (PyTri- derivatives vs Eu^{3+}, Am^{3+} and Pu^{4+}) were investigated by means of two well-established experimental techniques, UV-Vis titration and ESI MS analyses.

As regards the results, PyTri-ligands are the strongest complexants: the $SF_{Eu/Am}$ values, obtained within the conditions of a simulated GANEX process, are higher than 300, and they are confirmed by stability constants (calculated by UV-Vis analyses), which points the 2:1 [PyTri-]/[M^{3+}] stoichiometry being the most favorable one, as also highlighted by the ESI-MS spectra. On the other side, 1,10-Phen and BTBP derivatives present lower $SF_{Eu/Am}$ values (about 20-30), obtained within the conditions of a simulated i-SANEX protocol, but the latter might be used as masking agents in a 1-cycle SANEX process. Given the excellent performance of the hydro PyTri-ligands, we are moving toward further experimental research (test on mix settler with real waste, achievement of a flow-sheet, radiolysis studies, etc.) to define the operative conditions for industrial applications. These results candidate this 'italian' extractants family as one of the most promising in the international hierarchy and contribute to the global strategy of nuclear fuel reprocessing.

DEVELOPMENT OF NANOSTRUCTURED RHODIUM FILMS FOR DIAGNOSTIC MIRRORS EMPLOYED IN NUCLEAR FUSION SYSTEMS

Andrea Uccello - Supervisor: **Dr. Matteo Passoni, Dr. David Dellasega**

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

The thesis subject of this Ph.D in Energy and Nuclear Science and Technology (STEN) falls within the general topic of materials for nuclear fusion, one of the thematic areas of the Micro- and Nanostructured Materials Lab (NanoLab) of Politecnico di Milano. Specifically, it deals with the study and the development of nanostructured rhodium films for the production of diagnostic mirrors employed in nuclear fusion systems, like tokamaks. Considering the global energy scenario, nuclear fusion constitutes a potential and attractive alternative to the resources exploited up to now. It owns the capability to produce energy on a large scale, using plentiful fuels and releasing no carbon dioxide or other greenhouse gases. Relative to the magnetic confinement nuclear fusion, the most advanced tokamak experiment is ITER ("the way" in Latin), currently under construction. It aims to make a major step in the long-awaited transition from experimental studies of plasma physics to full-scale electricity-producing fusion power plants. The diagnostic system in ITER will play the crucial role of controlling the nuclear fusion process, ensuring at the same time the integrity of its toroidal chamber. Many diagnostics (about 30) will involve the use of the electromagnetic radiation emitted, reflected or diffused by

the thermonuclear plasma, which will reach the measurement apparatuses by complex mirrors labyrinths. Some of their most critical components will be the mirrors placed on the first wall of the ITER toroidal chamber, called First Mirrors (FMs). They will endure severe conditions in terms of intense thermal loads (up to 500 kW/m^2), strong radiation fields (up to 2×10^3 Gy/s) and high particle fluxes (neutron flux up to 3×10^{18} neutrons m^{-2}s^{-1}). Among the main effects of this harsh environment on FMs, this Ph.D thesis focused on FMs erosion by energetic particles coming from the hot plasma and on the re-deposition of sputtered first wall material transported in the plasma onto their surface. These phenomena could lead to a dramatic decrease of FMs specular reflectivity, posing a serious threat on the operation of the entire diagnostics. One of the principal materials investigated for FMs production is rhodium (Rh), thanks to its high reflectivity in a wide wavelength range, acceptable sputtering yield and melting point (1966 °C). The high cost of Rh as a raw material, together with the potential interest towards FMs solutions based on thin film technology, suggests its use as a high reflective coating deposited on a suitable substrate.
This Ph.D project had a twofold goal. Firstly, the

production of Rh coatings for FMs by means of Pulsed Laser Deposition (PLD) was addressed. By suitably changing the process parameters, PLD allows morphology and nanostructure control of the growing film in a peculiar manner with respect to the other deposition techniques, like electrodeposition and magnetron sputtering. This feature could in principle determine a potential improvement of Rh films response to the phenomenon of thermonuclear plasma erosion. The second part of this Ph.D thesis was devoted to a first study of the laser cleaning technique as a potential method to mitigate the re-deposition of first wall eroded materials onto FMs. The main objective was to develop a novel approach to the process of Rh films production-contamination-cleaning, in which the same laser system is exploited to experimentally investigate the topic of ITER FMs re-deposition with laboratory-scale facilities.
This Ph.D project was mainly experimental. The emphasis was addressed to basic aspects of the material science theme in order to establish new useful knowledge for the development of suitable solutions for realistic devices.
To achieve the first objective of this Ph.D thesis, the main intrinsic PLD drawbacks, that are the non-uniform and

heterogeneous nature of the deposit, the particulate and droplets production onto its surface, film-substrate adhesion and stress relaxation concern for thick coatings, were dealt with. The PLD deposition process was optimized in order to produce Rh coatings with a high specular reflectivity on a significant side area of 10 cm^2. In particular, the deposition of homogeneous planar films on wide surfaces was achieved by the so-called "off-axis" deposition technique. Ablation adopting high fluence (10-19 J/cm^2) infrared laser pulses limits droplets formation, assuring low diffuse reflectivity. The critical issues of film-substrate adhesion and stress relaxation for films some microns thick were addressed producing and properly characterizing nanoengineered multilayered Rh coatings. This strategy constitutes an interesting and attractive solution as it is based on a mono-elemental approach. Suitable morphology and nanostructure control of the growing films, guaranteed by PLD, was successfully exploited to improve Rh coatings behaviour under erosion of a pure deuterium plasma with some properties relevant for ITER (experimental campaign at the Physics Department of Basel University, Basel, Switzerland). In detail, specular reflectivity of Rh films with a granular-like morphology and small mean

crystallite size (6 nm) maintained rather constant during exposure. This phenomenon could be due to the lacking in the formation of rhodium deuteride (RhD$_x$, $x \leq 2$) sub-superficial layer.
The second part of this Ph.D thesis was devoted to the study of the re-deposition of first wall contaminants onto FMs; a novel approach to address this issue with laboratory-scale facilities was developed and preliminary tested. In particular, carbon and tungsten carbide "tokamak-like" contaminants were successfully produced by PLD and deposited onto Rh film mirrors. The PLD apparatus was properly modified in order to perform the laser cleaning process. With the aim of treating the overall Rh films surface (~10 cm^2), a sample handling procedure was also developed. Rh coatings were cleaned from carbon "quasi-film" by means of a double wavelength approach, i.e. a first scan with infrared laser pulses and a second scan with ultraviolet pulses. The achieved specular reflectivity recovery was satisfactory on a wide wavelength range (300-1800 nm). In order to demonstrate the effectiveness and robustness of the elaborated laser cleaning procedure, another tokamak-like carbon film, characterized by a low adhered compact morphology, was removed from Rh coatings. Mainly because of the scarce mechanical properties

of this carbon contaminant, a single scan with infrared laser pulses was sufficient to totally restore Rh mirrors specular reflectivity. The extension of the laser cleaning activity to the case of PLD tungsten carbide contaminants constitutes one of the first possible perspectives of this Ph.D thesis.
In the perspective of acquiring realistic information about tokamaks re-deposits in order to produce them faithfully by PLD, the study of the most recurring features of tokamaks contaminants from literature was also integrated with the latest results, obtained in the frame of a three months period at Joint European Torus (JET) tokamak (Culham, Oxfordshire, United Kingdom), of post mortem characterization of JET plasma facing components, or tiles, extracted after 2011-2012 experimental campaign. Among the main post mortem characterization techniques, tiles profiling permits to evaluate the erosion and re-deposition pattern of JET tiles on a macroscopic scale. In this frame, an interpretative tool (i.e. MatLab routine) for tiles profiling measurements was developed to face the main concerns related to this technique. The elaborated code was finally applied to profiling measurement results of JET divertor tiles.