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DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Coordinator:
Prof. Vincenzo Dossena

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:

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MECHANISTIC MODELING OF FISSION GAS BEHAVIOR IN CONVENTIONAL AND ADVANCED NUCLEAR FUELS

Tommaso Barani - Supervisors: Lelio Luzzi, G. Pastore, P. Van Uffelen

This thesis work deals with the development of mechanistic models of Fission Gas Behavior (FGB) for the analysis of conventional and advanced nuclear fuels, and their application to Fuel Performance Codes (FPCs). To correctly represent fuel performance various, intricate, and interrelated phenomena must be modeled to predict the evolution of material properties and microstructure, which in turn strongly affects the thermo-mechanical analysis of the nuclear fuel rod. Modeling of FGB is a fundamental step to predict the performance of nuclear fuels under irradiation, given its role in determining the thermo-mechanical condition of fuel rods and potentially affecting fuel rod operation in reactor. The primary role of FGB in determining the nuclear fuel rod performance in both Light Water Reactor (LWR) and Fast Breeder Reactor (FBR) conditions is confirmed by its investigation in the framework of different international research projects. Among them, this thesis work grafts on the Investigations Supporting MOX Fuel Licensing for ESNII Prototype Reactors (INSPYRE) H2020 European Project, the SciDAC project of the US DOE, and an International Nuclear Energy Research Initiative (I-NERI) collaboration project between US DOE and EURATOM involving POLIMI, Joint Research Center (JRC) Karlsruhe, and Idaho National Laboratory (INL). In this work, I leverage a multi-scale mechanistic approach to represent FGB, demonstrating how this modeling technique is suitable: (i) to describe some aspects of FGB in transient/high burnup conditions in conventional UO_2 nuclear fuel, which have been neglected so far for application in FPCs, in an original manner; (ii) to develop an original description of FGB in a fuel material – U_3Si_2, a candidate accident-tolerant material to replace UO_2 in conventional LWR – of recent consideration for use in power reactors. More in detail, the phenomena I tackled in this thesis are:

- The coarsening of intra-granular bubbles in UO_2, which could be responsible for a conspicuous part of fuel swelling in high temperature transients and high burnup conditions.
- The restructuring of oxide fuels microstructure at high local irradiation damage (HBS formation), accompanied by a peculiar intra- and inter-granular FGB with strong implications on local fuel swelling.
- The evolution of intra- and inter-granular bubbles in U_3Si_2 and resulting FGB.

Being conceived for engineering-scale FPCs, the models enforce a more detailed description of the underlying physical phenomena, while retaining a degree of complexity in-line with the computational requirements of FPC application. The development strategy I followed in this work to effectively pursuing the goals of the thesis followed a common route among the different models for the development phase, whilst it was twofold for the assessment phase. As for the development side, I implemented and verified all the models in the stand-alone computer code SCIANTIX, currently under development at POLIMI and of which I am one of the main authors. This code is a meso-scale code, describing FGB at the level of the fuel grain, meant for model verification, validation against local measurements, and designed to be included in existing FPCs in a multi-scale coupling scheme. As for the assessment against experimental data, I compared stand-alone model predictions when local measurements were available. For the U_3Si_2 FGB model, a significant experimental database is not available, due to the new conception of this fuel system for use in power reactors. Thus, I performed a comprehensive sensitivity and uncertainty analysis on the model parameters to support the conclusions of this work and to guide future research efforts, since an integral assessment against ongoing experiments is not yet achievable. The models developed in this thesis work surpass critical constraints of state-of-the-art FPCs. In fact, the new models consider critical FGB phenomena that are currently neglected in FPCs, albeit being very important in determining fuel performance under irradiation. Moreover, the description of FGB in U_3Si_2 constitutes a pivotal step towards the analysis and design of this fuel system for use in LWRs. Lastly, the model development followed a multi-scale approach, i.e., integrates information derived at atomic scale into the developed models conceived for application in FPCs. This aspect is a key component of the followed approach, allowing to infer model parameters which would be impossible to derive from experiments, and represents the only method to speed up model development for novel fuel systems. As evolution equations account for physical phenomena, the modeling strategy allows for effectively transferring the models to other materials with minor modifications in the physical parameters but preserving the fundamental equations. In this picture, the application of the developed models for UO_2 to other oxide fuel systems such as MOX or $(U,Pu)O_2$ or U_3Si_2 is of sure interest, together with the application of U_3Si_2 models to metallic fuel concepts (e.g., to U-Pu-Zr) alloys considered for application in sodium fast reactors. I introduced the developed models in engineering-scale FPCs, namely TRANSURANUS, developed at the JRC Karlsruhe, and BISON, developed at INL, under the aegis of a long-lasting collaboration between POLIMI, JRC-Ka, and INL.
To summarize, the main outcomes of my PhD thesis work are:

- The development and validation of more mechanistic models aimed at filling gaps in the state of the art to describe FGB in UO_2 in extreme conditions (i.e., high temperature transients and high burnup conditions).
- The development of mechanistic models describing FGB in a novel, accident-tolerant fuel material (U_3Si_2) to boost its design and analysis phase.
- The introduction of the developed models in engineering-scale fuel performance codes. The models are made available to the codes either via a direct implementation into the code itself (which is the case of the models introduced in the BISON code), either via the coupling of SCIANTIX with the TRANSURANUS code.

The latter bullet represents the main outcome of this thesis work from an engineering perspective, i.e., providing fundamental tools for the analysis of nuclear fuel behavior to FPCs. As for future developments of the presented work, many routes arise. First, the models may be complemented with helium behavior models. This aspect becomes of the greatest importance when U-Pu mixed oxide fuels (possibly bearing minor actinides as Np or Am) are considered, for both in-pile and storage conditions. Moreover, a comprehensive model for fission products behavior calls for the inclusion of non-inert fission products which can be found in the gas phase at certain temperatures (like Cs or I), and more in general the integration of FGB models to a thermochemical description of the fuel system. Second, the HBS model could be developed in the present formulation by considering two-species (gas atoms and vacancies) master equations as a starting point for the Fokker-Planck expansion. Indeed, it could be complemented with a description of the release of fission gas stored in the HBS porosity under accident conditions, e.g., in loss of coolant accidents or reactivity-initiated accidents. Third, as computational or experimental evidences on HBS formation in uranium silicide would arise, an application of this model to the analysis of high burnup uranium silicide fuel is of interest, as well as HBS modeling inclusion in the analysis of fast reactor $(U,Pu)O_2$ fuel. As for the assessment side, comparison of the models included in FPCs against integral irradiation experiments would help to assess the impact of these models on the overall fuel rod thermo-mechanical analysis. On the other hand, the comparison of stand-alone calculations of SCIANTIX to other meso-scale codes would be an important step to assess the predictive capabilities of the codes and possible development routes.

ENGINEERING OF TITANIUM OXIDE AND NITRIDE NANOSTRUCTURES FOR PLASMONIC APPLICATIONS

Beatrice Roberta Bricchi - Supervisor: Andrea Li Bassi

Plasmonics is a fascinating field which offers the attractive potential of manipulating light at the nanoscale. Plasmonic response occurs when an electromagnetic wave (e.g. solar radiation) interacts with a metal and, as a consequence, the conduction electrons resonate with the incident electric field, giving rise to collective oscillations. Interesting possibilities arise when considering plasmonic phenomena at metal-dielectric interfaces, in which surface plasmon polaritons (SPP) are originated, or in assemblies of metal nanoparticles, resulting in localized surface plasmon resonance (LSPR). These phenomena involve the strong intensification of the electric field close to the metal surface and the sub-wavelength confinement of light. These peculiar features make plasmonics appealing for several application fields, such as for imaging below diffraction limit by near-field spectroscopy, sensing and nano-sensing up to single molecule recognition, surface enhanced Raman scattering (SERS), waveguides and photoconversion. For the latter, the device efficiency could be improved by incorporating plasmonic functionalities into the photoanode; this is usually made of semiconducting oxide materials (e.g. TiO_2) which are responsible for the light absorption aimed at charge carrier separation, that can be employed for electricity production (i.e. photovoltaic cells) or chemical reactions (i.e. photocatalysis). A possible improvement approach includes the integration of noble metal nanoparticles (NPs) (e.g. Au and Ag), whose plasmonic properties are known to be tunable through their size distribution, density, shape as well as surrounding dielectric medium.

However, noble metals are not the best choice for any plasmonic application. Indeed, metals exhibit high optical losses in the infrared, restricting possible applications in this range, together with the difficulty of finely tuning their optical properties, limiting the development of devices such as optical modulators. In addition, some technological challenges arise for the industry application of metallic materials due to poor hardness, low chemical stability and resistance to high temperature, as well as the difficulty in the realization of ultrathin metallic films (i.e. film thickness of few nanometers, appealing for sub-wavelength optical structures and nanoelectronics) and non-compatibility with standard silicon manufacturing process (i.e. complementary metal-oxide semiconductor, CMOS). In response to such limitations, different classes of materials have been proposed as an alternative. Transparent conductive oxides (TCOs) are doped oxides widely employed as transparent electrodes for many optoelectronic applications. TCOs have been recently studied in the plasmonic field because they have demonstrated a tunable plasmonic response in near-IR and mid-IR range depending on carrier density, which is controlled in turn by adding dopants or by engineering oxygen defects. Among TCOs, $Ta:TiO_2$ has been already demonstrated to be a performing oxide with low resistivity and high mobility, while ensuring the advantages of TiO_2, i.e. low-cost, non-toxicity and chemical stability. Another alternative to noble metals involves transition metal nitrides. Among them, titanium nitride (TiN) is a unique material which goes beyond the aforementioned limitations, providing a tailored plasmonic response in the visible and near-IR range which in principle can be controlled through stoichiometry and crystalline quality. Metal nitrides are refractory, stable and hard materials and have the technological advantage to be currently used in CMOS technology. Finally, the study of alternative plasmonic materials paves the way to other applications, e.g. in the field of IR vibrational spectroscopy, waste heat management, sensors and telecommunications.

In such context, this PhD thesis project concerns an experimental investigation aimed to the development and the investigation of nanostructured thin films based on titanium oxides and nitrides, focused to achieve a fine control of their physical properties (i.e. morphology, structure, composition) as well as the understanding of the material optical and electrical behavior and their potential application in the plasmonic field. The specific systems investigated were Au NPs integrated with TiO_2 nanostructured thin films and thin films and NPs assemblies based on alternative plasmonic materials, namely $Ta:TiO_2$ and TiN. These systems were grown via physical vapor deposition techniques, in particular pulsed laser deposition (PLD), followed by post-deposition thermal treatments to crystallize the materials in the desired phase, or to modify their functional properties. The properties of the obtained systems were studied with a focus on the optical and electrical response and their relation with the system structure, from atomic to nano/masoscale, aimed to understand and to optimize the system behavior in view of possible plasmonic applications.

For Au NPs integrated with TiO_2 hierarchical films, the successfully integration was possible with an original single-step pulsed lased co-deposition procedure, leading to Au NPs homogeneously dispersed through the whole thickness of the TiO_2 film. The control of process parameters allowed a fine tuning of film properties in terms of porosity, crystalline structure as well as Au NP size and number density, which in turn affect the optical response, giving the possibility of controlling Au NP plasmonic resonance over a certain range. The high porosity was interesting for several applications, indeed preliminary tests of photocatalysis and SERS experiments have been performed leading to promising results.

For $Ta:TiO_2$ thin films, after the first step of optimization of the synthesis parameters, the properties were studied as a function of Ta content (5 and 10% at.) and thickness (down to ultrathin films), with a focus on the understanding of electrical and optical behavior. Conductive films were obtained down to 10 nm. The high dopant activation efficiency demonstrated by Ta-doping offers the possibility of fine tuning both electrical and optical properties by handling Ta content, while the plasma frequency of $Ta:TiO_2$ films was estimated to be in the near/mid-IR range. Then, a preliminary study of complex $Ta:TiO_2$-based systems involved Au NPs integrated in compact $Ta:TiO_2$ thin films (aimed to tune the visible plasmonic frequency of Au NPs by changing the dielectric constant of the surrounding TCO matrix) and $Ta:TiO_2$ NPs assemblies in thin films.

For TiN thin films, the correlation between synthesis process parameters with morphology (from compact-columnar to nanoporous tree-like and to foam-like) and stoichiometry/composition was established, while the met oxidation-issue was handled with different strategies depending on film morphology. Nanoporous hierarchical films formed by TiN (or TiO_xN_y) NPs assemblies were successfully obtained thanks to a specific investigation on PLD mechanisms with in-situ characterization techniques. For particular synthesis conditions, NPs assemblies exhibited an excellent broadband absorption along a wide optical range (promising for solar energy harvesting and hot electron devices). The employed post-deposition thermal treatments promoted a slight crystallization of the films, while resulting a good way to tune optical response.

As a perspective, $Au-TiO_2$ systems can be exploited for other plasmonic applications, especially those requiring nanoscale porosity and light scattering, while the potentiality of the employed integration approach can be extended to other NP/oxide systems with controlled properties. The resulted tunable optical and electrical behavior of $Ta:TiO_2$ and TiN thin films paves the way to applications usually unaffordable for noble metals, moreover they can be employed as building blocks for sub-wavelength optical structures (metameterials) with engineered plasmonic behavior and for nanoelectronics.

A MULTI-PHYSICS MODELLING APPROACH FOR THE ANALYSIS OF BURNUP CALCULATION OF THE NEXT GENERATION OF NUCLEAR REACTORS

Christian Castagna - Supervisors: Antonio Cammi, Daniela Cancila

In nuclear reactor analysis, multi-physics approaches are related to different computational and numerical methods that couple neutronics and thermal-hydraulics, strongly interrelated in nuclear systems.
The recent interest in multi-physics approaches is justified by the growing need for advanced analysis to improve the efficiency and the safety of the operating power plants. These approaches are further important to study the Next Generation of Nuclear Reactors, where their complexity and peculiar aspects require the development of accurate simulation tools. In addition, advanced analysis avoid the installation of expensive experimental facilities, obtaining research results at a lower cost in a shorter period. Furthermore, their validation with available data allows the reinterpretation of results from old experiments.
The current multi-physics approaches usually employ low fidelity models, since some approximations in governing equations of each physics phenomenon are adopted, as in neutronics deterministic codes and subchannel codes.
Recently, high-fidelity models have been developed with Monte Carlo codes for neutronics and Computational Fluid Dynamics (CFD) codes for thermal-hydraulics. They assure high accuracy and flexible implementation to model different reactor geometries. In particular, CFD allows characterizing local conditions of the fluid, to study specific thermal-hydraulics phenomena as fluid instabilities, turbulent mixing or natural circulation.
In burnup analysis, a high-fidelity multi-physics characterization allows understanding accurately the influence of the correct temperature distribution and other physical parameters, that have remarkable effects on fuel consumption. The improvement of burnup analysis tools aims to reduce uncertainties and design limits for fuel management, to decrease the economical costs and improve the fuel cycle.
In this context, the theme of the thesis concerns the development and assessment of high-fidelity multi-physics tools for burnup analysis.
In the first part, I developed a coupling between the Serpent Monte Carlo code for neutronics and the OpenFOAM toolkit for thermal-hydraulics. I implemented the procedure on the burnup history of a 3D PWR fuel pin. I obtained, from comparisons with data reported in the literature, the agreement with neutron flux and fuel/coolant temperature distributions over time. The procedure has been able to reproduce the physical effects from the mutual feedback between neutronics and thermal-hydraulics, i.e. axial asymmetric shape of fission rate and fuel temperature, flattening of axial fission rate and fuel temperature over time, radial fuel temperature on self shielding. The local burnup has shown not negligible differences for axial and radial fuel consumption, in comparison with a uniform (non-coupled) case. Since the model reproduces a clean and simplified condition of a PWR pin, these may be minimum variations. If the operational conditions are considered, the multi-physics effects may be higher, since they add up to other sources of uncertainties, like control rods movements, change of position inside the reactor core, change of thermal power and nuclear data.
In the second part, I extended the multi-physics approach to FA (fuel assembly) and full core designs.
For the former, I simulated the central FA of ALFRED (Advanced Lead-cooled Fast Reactor European Demonstrator), in the framework of the collaboration with ENEA (Ente Nuove tecnologie per l nergia e l mbiente) concerning the development of numerical tools for the LFR design and safety analysis.
I performed the coupling for a sixth subassembly, proving the reliability to employ symmetries to reduce the geometry simulated. I reproduced the design parameters for neutronics and thermal-hydraulics, verified by code-to-code comparisons with previous works in literature.
For the full core design, I applied the multi-physics coupling to the TRIGA Mark II reactor of the University of Pavia. This activity is part of the framework of ARCOFAST (Analysis of Reactor Core-Fast neutrons Analysis with Simulations and Tests) project, coordinated by INFN (Instituto Nazionale di Fisica Nucleare) in collaboration with the University of Milano-Bicocca. I developed, verified and validated the multi-physics model of the first criticality configuration.
In neutronics, I validated the model through a benchmark analysis with experimental criticality configurations and control rods calibration. In thermal-hydraulics, I obtained the correct temperature and velocity fields, comparing the results with experimental and simulation data reported in literature. Furthermore, the model has been able to reproduce the local effects of the control rods on the fuel temperature distribution.
In the third part, I proposed a solution to the problem of the computational cost, by developing and implementing a new methodology for burnup analysis, based on Reduced Order Methods (ROMs). The philosophy behind ROMs is that the behaviour of a physical system is well described by a small number of dominant modes, allowing to reduce the degrees of freedom of the original problem. Among different techniques, I adopted the Proper Orthogonal Decomposition (POD) that is one of the most valuable methods in the ROM framework. POD has the powerful capability to select the most energetic modes that represent the main significant features of the system. I implemented and assessed the methodology on burnup analysis of the 2D TMI-1 PWR cell, described in the OECD benchmarks for UAM (Uncertainty Analysis in Modelling) of LWR. I reproduced the criticality and the concentrations of the FOM (Full Order Model) over time, where the method is based on the reconstruction of burnup matrices from a linear combination of POD basis functions. Moreover, I implemented the reconstruction of the nuclide concentrations among different steps (without burnup) and I run criticality calculations, that resulted in a good approximation of keff. I also provided a physical interpretation of POD basis functions respect with the original physics problem.
The results obtained pave the way for further developments in several directions.
A first one is the implementation of the multi-physics coupling for full core analysis of PWR. Thanks to the wide availability of experimental data, it is possible to validate the procedure to industrial reactor designs.
A second direction is to exploit the multi-physics approach to study complex phenomena in CFD. The characterization of the local fluid conditions allows analyzing flow instabilities, turbulent mixing and natural circulation, that have a reliable impact on safety. These studies are important in the Generation IV reactors, where the determination of the thermal-hydraulics conditions, concerning neutronics, is a key issue of their assessment. The start point can be the study of the natural circulation of the TRIGA Mark II reactor, by including the upper pool in the full CFD problem.
A third direction is the extension of the ROM to the burnup analysis in FA and full core calculations, verifying and validating the method through benchmark analysis. It is crucial to limit the computational cost in the offline stage, to run the reduced model as many times as required. The assessment of this procedure opens the possibility to burnup calculations with lower cost to perform sensitivity analysis for nuclear data uncertainties. The latter is of great interest in the evaluation of the accuracy of the input/output data in modelling depletion capabilities.
Finally, it is important to standardize the developed approaches in simulation software. This provides the possibility to many users for testing and optimization, to make these tools flexible for reactor analysis.

AN INNOVATIVE MULTIPHYSICS MODELLING APPROACH FOR THE ANALYSIS AND THE DEVELOPMENT OF THE GENERATION IV MOLTEN SALT FAST REACTOR

Eric Cervi - Supervisors: Antonio Cammi, Lelio Luzzi

The theme of the PhD thesis is the improvement of the multiphysics modelling of the Generation IV Molten Salt Fast Reactor (MSFR), developed in the frame of the Euratom H2020 Projects SAMOFAR and SAMOSAFER. Compared to traditional solid-fuelled nuclear reactors, Molten Salt Reactors (MSRs) have a distinguishing feature, namely the presence of a liquid fuel, which acts simultaneously as coolant. This peculiarity may lead to intrinsic improvements in the fuel cycle closure, reactor safety enhancement and plant simplification, but at the same time introduces specific design challenges, safety issues and technological constraints that are different from both conventional water-cooled reactors (e.g., Light Water Reactors, LWRs) and other fast systems (e.g., Liquid Metal Fast Reactors, LMFRs). Furthermore, the adoption of a helium bubbling system (i.e., the injection of helium bubbles to remove gaseous fission products and to control reactivity) constitutes a further complication for the numerical simulation of the Molten Salt Fast Reactor, as the impact of the gas bubbles on the system behaviour needs to be carefully investigated. Another specific issue of MSRs is represented by the fuel mixture compressibility which, introducing delays in the thermal expansion feedbacks, may have a strong impact on the system dynamics (especially in fast, reactivity-driven transients).

Since these issues are specific of circulating fuel reactors only, they were never taken into account in the analysis of traditional solid-fuelled systems. Consequently, simulation codes developed for LWRs and LMFRs cannot be retrieved for the analysis of the MSFR, and the development of new computational tools, tailored to the specificities of this innovative system, is required. In addition, state-of-the-art models of MSRs are also unsuitable to study the helium bubbling system and fuel compressibility effects, as they rely on single-phase, incompressible fluid-dynamics solvers.
In this context, a new multiphysics OpenFOAM model for the analysis and simulation of the MSFR behaviour is developed in the present thesis.
A two-phase, compressible thermal-hydraulics model is adopted in order to handle the presence of bubbles in the reactor and to account for the fuel mixture compressibility. The thermal-hydraulics model is coupled with two different neutronics models (multi-group neutron diffusion and SP_3 neutron transport) and with transport equations for the delayed neutron and decay heat precursors. The set-up of this tool constitutes a challenging task, requiring:

- the development of specific models (both from a theoretical and numerical point of view) for each physics that comes into play;
- the development of a coupling strategy to catch the interplay between all the different physics and to properly solve the coupling non-linearities.

Thanks to the new multiphysics simulation tool, the helium bubbling system and fuel compressibility effects have been studied, highlighting phenomena that have never been observed with state-of-the-art tools.
Concerning the analysis of the helium bubbling system and its effect on reactivity, the main results of the thesis can be summarized as follows:

- The void reactivity feedback of the bubbles is strongly influenced by spatial and neutron importance effects. Consequently, an accurate evaluation of the bubble spatial distribution inside the reactor is fundamental for a correct evaluation of reactivity and of the void coefficient.

- Simply assuming a uniform bubble distribution (i.e., modelling the void fraction as a uniform density effect) as made by state-of-the-art, single-phase models leads to a significant underestimation of the void coefficient. In case of a sudden decrease of the void fraction (e.g., following a failure of the bubble injection systems), the resulting positive reactivity injection would be underestimated as well. Consequently, the “uniform bubble distribution” approach is strongly non-conservative for the analysis of accidents involving rapid reductions of the bubble concentration.

- The same results are observed with three different neutronics models (multi-group neutron diffusion, multi-group SP_3 transport and, for verification purposes, via a coupling with a continuous energy Monte Carlo code). This points out that the outcome of this analysis is not dependent on the choice of the neutronics model but represents a physical effect that can only be observed by means of a two-phase fluid-dynamics solver. The good agreement obtained among the three different approaches also constitutes an important verification for the developed neutronics models and for the coupling strategy with the thermal-hydraulics herein adopted.

- A sensitivity analysis to bubbly flow closure relations for the evaluation of the bubble diameter and of the interphase momentum and heat transfer points out that results are not significantly affected by the choice of these correlations. Consequently, the conclusions presented in this thesis are solid and reliable, as far as bubbly flow closure relations are concerned.

On the other hand, concerning the analysis of fuel compressibility effects, the following main conclusions can be drawn:

- The fuel mixture compressibility has a strong impact on the system dynamics, introducing delays in the thermal expansion reactivity feedbacks. This is particularly relevant in rapid, super-prompt-critical transients, in which the characteristic times of neutronics and of pressure wave propagation through the reactor are comparable.

- Due to the delay introduced by compressibility, the energy released during fast transients is higher, compared to the predictions of incompressible models. Consequently, state-of-the-art approaches not accounting for the fuel compressibility are not suitable for a conservative analysis of super-prompt-critical accidental scenarios.

- The presence of gas bubbles inside the reactor modifies the fuel compressibility both locally and globally, leading to further effects that cannot be caught with standard single-phase models. In more details, the bubble distribution needs to be known with accuracy to correctly predict the propagation of the wave-front and of the transient evolution in turn. Therefore, the problems of the helium bubbling system and of fuel compressibility must be studied together.

In the light of these conclusions, the present work constitutes a substantial step forward compared to state-of-the-art modelling approaches for the MSFR, from a methodological point of view as well as in terms of results. The outcome of this analysis opens the way to many different research directions:

- A first, interesting development could be a detailed analysis of the fluid-structure interaction between the fuel mixture and the reactor walls. This investigation would serve two different purposes. On one hand, it is necessary to assess if the structural integrity of the walls can be challenged by the strong pressure waves arising in super-prompt-critical transients. On the other hand, wall deformation effects may have an impact on the reflection and transmission of the waves, leading to further effects on the system dynamics.

- Thanks to the availability of a two-phase fluid-dynamics model, fission gas generation and extraction, as well as the formation of metal precipitates and their transport through the system, can be a further topic to be investigated in the future. This activity is planned in the SAMOFAR follow-up project, SAMOSAFER.

- The development of reduced order models can also be of interest to reduce runtimes, facilitating the optimization of the reactor design (thanks to the possibility to run multiple and faster simulations) and paving the way to real-time control applications.

A COMPUTATIONAL FRAMEWORK FOR MODELING, SIMULATION AND OPTIMIZATION OF ENERGY SUPPLY CHAINS

Shiyu Chen - Supervisors: Enrico Zio, Wei Wang, Michele Compare

Energy Supply Chains (ESCs) are complex systems made up of a number of heterogeneous components/agents interacting with each other, the environment, its hazards and threats. The components/agents are structured in a hierarchical system, within which they operate and cooperate in a balanced transaction environment to realize the maximization of the benefits, under various environmental and safety constraints. ESCs significantly contribute to the sustainment of many industrial areas, such as biomass, oil and gas, chemical processing, sustainable and renewable energy, etc.

However, ESCs are challenged by multiple sources of uncertainties and risks. Uncertainties exist in supply and demand, propagate through the interactions over the whole ESC and influence the agents profits and the ESC operations. Due to the uncertainties, the risk of supply failure is difficult to predict. In such situation, ESCs must offer enhanced flexibility, innovative connectivity and communication, to guarantee an orderly and healthy supply management, so as to sustain the operation of the energy industry.

The objectives of the Ph.D. work are to develop a modeling framework for ESC process modeling simulation and optimization, which includes: 1. ESC modeling to identify, understand and analyze the complex interactions and for the evaluation of the resilience of ESCs. 2. ESCs efficient production planning optimization under multiple sources of uncertainty. 3. ESCs production planning considering risk of supply failure. 4. Solving the Many-objective Optimization Problem (MaOP) caused by the different agents for efficient production planning of ESCs.

With respect to the objective 1, an Agent-based Modeling(ABM) approach is proposed for modeling and simulating ESCs of the oil and gas industry, capturing the peculiarities of its diverse interacting elements, such as plants, refineries, storages, etc. Different disruption scenarios and recovery strategies are considered in the Agent-based ESC model for investigating the relevant factors influencing ESC resilience.

With respect to the objectives 2 and 3, a simulation-based Multi-Objective Optimization (MOO) framework for ESC production planning is developed. The ABM simulation is embedded into a Non-dominated Sorting Genetic Algorithm (NSGA-II) is then adopted for identifying the Pareto solutions. For ESCs with uncertainties and changing structures, the ESC total profit is maximized and the disequilibrium among the agents' profits is minimized. Moreover, considering disruption risks, the ESC total profit is maximized and ESC risk under uncertainties is minimized.

Furthermore, an improved Cooperative Co-evolutionary Particle Swarm Optimizer (CCPSO) is proposed to solve the Many-objective Optimization Problem (MaOP) in the agent-based ESC model. The variables are decomposed into different species based on agents relationships and allowed to evolve independently during the optimization process. Each species has its own repository to keep a historical record of the nondominated vectors in which the solutions are evaluated and updated by cooperating with other species. The effectiveness of CCPSO is proven by test functions and a case study.

ADVANCED QUASI-OPTICAL COMPONENTS FOR FUSION-REACTOR- RELEVANT ELECTRON CYCLOTRON SYSTEMS

Francesco Fanale - Supervisors: Alessandro Bruschi, William Bin

This work has been carried out in collaboration with the Institute of Plasma Science and Technology of the National Research Council (ISTP-CNR) and deals with the design of a set of First Plasma (FP) protection components for the FP operations of the International Thermonuclear Experimental Reactor (ITER), needed for the injection of electromagnetic waves resonant with the Electron Cyclotron (EC) frequency to assist plasma breakdown. These components consist of two mirrors and a diffraction grating designed to provide the prescribed trajectory and parameters of the EC beams coming from an upper launcher to the resonance, where they will interact with electrons causing plasma breakdown and being partially absorbed. The residual radiation is then trapped and dissipated in the beam dump to protect the port plug walls and to reduce the stray radiation inside the vessel.

For the design of the mirrors, a code in Matlab based on the Gaussian beam theory in vacuum has been developed for the evaluation of the parameters of the beams during propagation to define the optical surface of the mirrors. The results, have been implemented in CATIA to generate a 3D model with the purpose of following the propagation of the single-beams inside the vacuum chamber, towards the plasma resonance and finally to the beam dump. For two of the three mirrors, the shaped surfaces obtained are a portion of ellipsoid of revolution and a section of two-sheet hyperboloid of revolution. For the third mirror, the dimension, direction of propagation and astigmatism of the injected beams forced to opt for a diffraction grating. For the description of the beams after the grating, the code in Matlab has been modified including an additional transformation of the beams to simulate the effect of the grating on the dimension of the beams after reflection. The quasi-optical design of the grating required the definition of the desired direction of propagation and of the parameters of the reflected beams that have been then provided to the Institute of Interfacial Process Engineering and Plasma Technology (IGVP) of the University of Stuttgart, which was in charge of the design and optimization of the profile of the grating grooves. A parametric model in CATIA has been included in the 3D model for the evaluation of the direction of propagation of the beam axes based on the conical off-plane diffraction equation, using the parameters of the grooves obtained by IGVP. The resulting design of the mirrors has been compared with the results obtained with the electromagnetic simulations software GRASP, showing a good agreement.

A first order tolerance analysis of the mirrors has been carried out to evaluate the effects of either possible offset and misalignments of the mirrors during installation or different focal lengths of the shaped mirrors. The tolerances of the overall system have been calculated considering a statistical approach, to take into account the random combination of the single contributes.

The analysis has been done developing a parametric model in CATIA.

The dump consists of five metallic plates arranged in a box configuration in which a first purely reflective plate with properly shaped groves spreads the high incident power density of the beams (up to 40 MW m^{-2}), while the other plates are covered with a ceramic coating of proper thickness for a controlled absorption of the power, multi-reflecting inside the box. The selected coating was studied in the past by the ISTP-CNR and has been tested as absorbing layer in calorimetric loads designed for the commissioning of the ITER gyrotron sources. For the definition of the proper distribution of the coating, a multi-bounces model has been developed in Matlab based on geometrical optics. In the model, each Gaussian beam has been discretized in a bundle of many rays using an elliptical mesh with ellipses concentric to the spot ellipses of the beams at the dump. The path of each ray is followed bounce after bounce inside the dump, until the power carried by the single ray decreases down to a limit set to stop the simulation or until the ray escapes from the dump. The absorption factor has been evaluated using a model developed in the past by ISTP for the properties of the coating as a function of the incidence angle of the rays calculated at each bounce, the coating thickness defined during the design and the frequency of the wave, fixed and equal to the nominal one of 170 GHz. The final absorption factor distribution on the plates has been defined in order to respect a maximum absorbed power density on the coating of 2 MW m^{-2}, taken as a reference value, according to the experience gained in the past in the framework of the loads development. Fig.1 shows an example of absorbed power density distribution obtained with the multi-bounced model.

The design results in a reflectivity back to the vacuum chamber of ~3% of the total power, in compliance with the requirement of 10%. Having a good statistics on the dump surfaces requires the use of many rays: to have a reasonable computational time the power level set to stop each ray simulation was 500 mW. The power not correctly taken into account in this way is ~1.5% of the total. With a test done setting a power limit of 1 mW and considering a reduced number of rays to reduce computational time, the fraction of missing power is reduced to 0.07%, confirming the model correctness. A tolerance analysis has been carried out to consider either the non-ideality of any coating thickness deposition during the manufacturing or a shift of the incidence points of the beams at the dump due to offsets or misalignments of the mirrors. The final layout is shown in Fig.2.

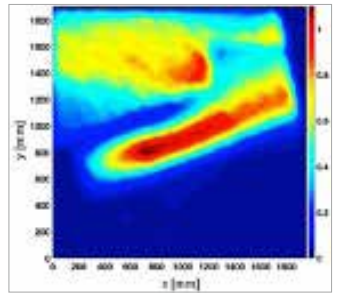

Fig. 1 - Example of the final absorbed power density distribution in MW m-2 for one of the side plates of the beam dump.

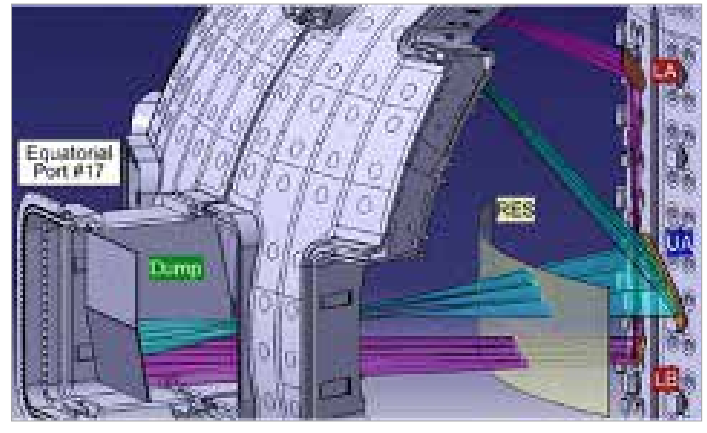

Fig. 2 -Final layout of the FP components. The propagation of the beams is also shown in magenta and cyan. The plasma resonance is represented with a yellow surface.

ADVANCES IN LASER-DRIVEN ION ACCELERATION THEORY

Arianna Formenti - Supervisor: Matteo Passoni

Ion acceleration by superintense laser pulses is of great interest for both fundamental research and applicative purposes. The concept of driving the acceleration with lasers is promising for the development of compact, cost-effective and versatile ion accelerators with properties relevant for selected applications, such as secondary radiation sources, materials characterization, plasma diagnostics. The complexity of the physical system -- comprised of a ultra-intense laser pulse irradiated upon a suitable target -- poses significant challenges that still need to be faced with the ultimate goal to get a better control of the acceleration process, so to be able to design optimized configurations for the applications. To this purpose, it is crucial to get a better understanding of the physics at play, addressing several key open issues. In this thesis, novel theoretical aspects of advanced schemes of laser-driven ion acceleration are investigated by means of analytical models and numerical simulations, within a cross-disciplinary framework where plasma physics, computer science, nuclear engineering and materials science are involved altogether. Improvements in the modeling of the most established mechanisms for laser-driven ion acceleration, i.e. radiation pressure acceleration and target-normal sheath acceleration, let us obtain new elements on important physical features, namely the reflection of a laser pulse by a thin foil and hot electrons non-equilibrium. Moreover, the development of dedicated numerical particle-in-cell simulations together with in-depth analyses allowed for further progress in the physical understanding of the non-conventional scheme of acceleration based on nanostructured low-density double-layer targets. Simulations revealed that the plasma nanostructure and morphology may play a significant role and influence several features of the physics at play during the interaction, such as laser absorption and species distributions. Considering these new insights, we numerically model a compact proton source based on a table-top laser system coupled with nanostructured targets. We assess the benefits due to the advanced targets and the potential for secondary neutron generation as a promising application.

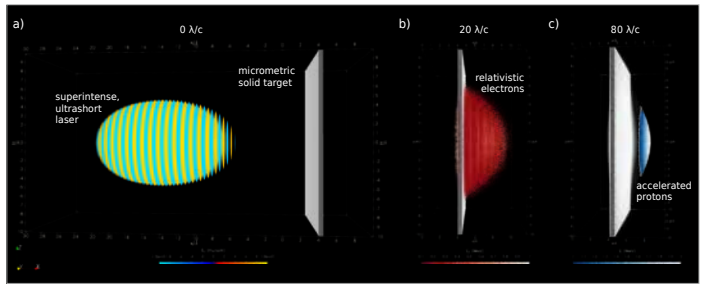

Fig. 1

HIGH TEMPERATURE NON-IDEAL COMPRESSIBLE FLOWS OF SILOXANE VAPORS

Simone Gallarini - Supervisor: Andrea Spinelli

Compressible flows of molecularly complex fluids operating at thermodynamic conditions close to the vapor saturation line and the critical point are of interest in various industrial applications. In the last two decades considerable advancements were made in the thermodynamic modeling and numerical simulation of highly non-ideal flows. However, experimental data are still scarce in the literature up to date, due to the hostile environment associated with such flows, that feature high temperature, high pressure, and possibility of fluid decomposition.
This thesis presents the first characterization by means of pressure, temperature and direct velocity measurements of a flow of a molecularly complex fluid operating at non-ideal conditions.
Tests were carried out on the Test Rig for Organic Vapors of Politecnico di Milano. A nozzle was selected as the simplest geometry of relevance for the study of fundamentals of the fluid-dynamics of such flows and for its representativeness of industrial applications, such as organic Rankine cycle turbines.
Siloxane fluids hexamethyldisiloxane (siloxane MM - $C_6H_{18}OSi_2$) and octamethyltrisiloxane (siloxane MDM - $C_8H_{24}O_2Si_3$) were chosen for testing due to their relevance in high temperature ORC applications. In literature, data about their thermal stability are scarce or absent, thus their behavior and decomposition at temperatures comprised between 200 °C and 420 °C was studied with a dedicated experimental campaign.
First, a method based on the deviation of the vapor-liquid equilibrium curve of the fluid measured before and after thermal stress was employed, but it yielded contradictory results, due to the low volatility of the tested fluids. Thus, an improved method was adopted, based on chemical analysis of both vapor and liquid phases of the sample subjected to thermal stress. MM proved to be more stable than MDM. Moreover, due to the current interest in the use of mixtures in ORCs, an equimolar mixture of MM and MDM was also tested, showing a behavior that appears to be different from the simple superimposition of pure fluid ones.
With the information about the thermal stability of working fluids, their non-ideal fluid dynamics was then characterized. Experimental observations of non-ideal flows by means of pressure and temperature measurements, complemented with schlieren visualizations (from which the Mach number was measured), are first presented. The dependence of flow quantities on total conditions is proved. However, for a complete characterization of the flow, the independent measurement of velocity is necessary. To reach this goal, the Laser Doppler velocimetry (LDV) technique was chosen and a specifically designed seeding system was implemented.
The adopted apparatus was conceived for seeding high temperature, high pressure and potentially condensible flows without contamination, and it is suitable to every application where at least some of these requirements are present.
The full characterization of a flow of a molecularly complex fluid operating at non-ideal conditions was carried out. Three different experimental cases are presented: a subsonic compressible nozzle flow with a large uniform region at Mach number equal to 0.7, a high velocity gradient supersonic flow at Mach number equal to 1.4 and a near zero velocity gradient flow at Mach number equal to 1.7. Temperature, pressure and direct velocity measurements are performed to characterize the flow at discrete points along the nozzle axis. Measured velocity is compared with both computational fluid dynamics (CFD) calculations and velocity computed from pressure and temperature measurements.
In both cases the thermodynamic model applied was a state-of-the-art Helmholtz energy equation of state. Maximum observed deviations between measured velocity and those obtained from CFD or computed from pressure and temperature measurements are below 6.6% and reduce to about 0% to 4% in most cases.
These are the very first direct measurements ever exploiting the LDV technique in a high velocity non-ideal flow and show the feasibility of laser Doppler velocimetry in this framework. This work poses the basis for a complete characterization of the flow with pressure, temperature and velocity measurements along the whole nozzle axis. Further, the LDV system presented in this thesis can provide reference values of velocity for the calibration of directional pressure probes in the non-ideal regime, that can be employed for the study of the fluid dynamics of linear blade cascades.

NON-EQUILIBRIUM SYNTHESIS OF NANOCRYSTALLINE TRANSITION METAL CHALCOGENIDES CATALYSTS FOR ELECTROCHEMICAL FUELS PRODUCTION

Giorgio Giuffredi - Supervisor: Fabio Di Fonzo

The increasing technological and scientific interest in the synthesis of carbon neutral energy vectors by electrochemical technologies, like hydrogen production through the hydrogen evolution reaction (HER) from water electrolysis or CO_2 reutilization into value-added chemicals through its electroreduction reaction (CO_2R), motivated intense research activity on electrocatalytic materials for these applications, focusing on non-metallic alternative catalysts that can overcome the drawbacks affecting the state-of-art transition and noble metal catalysts for the HER and CO_2R and still exhibit comparable activity. For the HER, the state-of-art Pt is expensive and scarce, while transition metal CO_2R catalysts suffer from the energetically unfavorable scaling relations limiting their maximum efficiency. Transition metal chalcogenides (TMDs) have emerged as one of the most promising an appealing family of non-metallic catalysts thanks to their polymorphism-dependent electrochemical properties and the dynamic character of their active sites, which show remarkable activity for the HER and CO_2R. Despite their high activity, the device-level performance of TMDs is hampered by two main drawbacks arising from their structural organization, which make their application technologically and economically unfeasible: a limited active surface area and an unsatisfactory electrical conductivity. For crystalline TMDs, the low active area is related to the localization of the active sites only on the edges of the layers of the material whereas the majority of it is inert, while the sluggish electrical conductivity arises from the inefficient inter-layer electron transfer in the 2D layered structure. For amorphous TMDs, the small surface area is related to usually employed wet-chemical synthesis method that grant limited control over the final morphology of the material (despite the higher density of active sites than the crystalline counterpart) while their disordered structure lacking a periodic atomic arrangement hinders an efficient electron transfer. This thesis work develops a novel design strategy for TMD-based catalysts that overcomes these drawbacks through a precise control on the structural and morphological characteristics of these materials over different length scales, to enable an efficient performance in operative conditions typical of real electrolyzer devices. The HER is chosen as a benchmark reaction to assess the effectiveness of this strategy, since it is the most studied electrochemical reaction for fuel synthesis and because of its simple and reversible nature, and three different TMDs are tested, namely molybdenum sulfide (MoS_x), tungsten selenide (WSe_x) and molybdenum selenide ($MoSe_x$). We show that the mesoscale morphological features like thickness and porosity influence the extrinsic catalytic parameters like onset potential and electrochemical active surface area, while the structural characteristics at the nanoscale influence intrinsic catalytic properties like turn-over frequency or reaction rate. This precise control over the material is achieved by the synthesis of self-supported nanostructured TMD catalysts exploiting the thermodynamic non-equilibrium characteristics of Pulsed Laser Deposition. The interaction between non-equilibrium, laser-generated plasma and the process gas during synthesis is studied thoroughly *in-situ*, showing how the plasma dynamics is affected by a drag force exerted by the background gas. By controlling the drag coefficient of the gas, we induce the nucleation of nanoparticles of material and control their kinetic energy upon their sequential attachment to grow the materials. In this way, the growth regime of the resulting structures is controlled and the mesoscale morphology of the synthesized material can be modified, resulting in TMDs with tunable morphologies from compact films with limited porosity to hierarchical nanostructures. At the same time, the growth of the nanostructured films by the sequential attachment of energetic nanoparticles confers them a peculiar nanoscale organization that is radically different from both crystalline and amorphous TMDs. By microscopy and spectroscopic analyses, we show the nanocrystalline organization of the pristine PLD-grown TMDs, where in an amorphous matrix are embedded defective nanodomains composed of distorted and bent 2D layers with a short-range periodicity. This pristine nanoscale organization transitions to the actual catalytic structure through an electrochemical activation process, with a series of modifications common to the three studied TMDs: a reduction of chalcogenide ligands and a surface oxidation. These modifications foster the formation of under-coordinated surface sites with high activity, change the metal-chalcogen ligands configuration thus altering the electronic structure, and form different surface oxide phases which improve the electron transfer characteristics. The high HER activity of this nanoscale organization is confirmed by the very high per-site TOF of 2.4 H_2 s^{-1} that characterizes the WSe_x catalysts at -10 mA cm^{-2}, and by the very fast reaction rate of the MoS_x catalysts, with a remarkable Tafel slope of 35 mV dec^{-1}, which overcomes the 40 mV dec^{-1} threshold for the reaction rate on other molybdenum sulfides, indicating a faster electron transfer than other MoS-based catalysts and reaching comparable kinetics to the most active metallic catalysts. Leveraging on this high intrinsic activity, an electrochemical parametric analysis shows how tuning the mesoscale morphology of the nanostructures optimizes the surface area and the charge transfer resistance, reaching overpotentials at -10 mA cm^{-2} as small as 126 mV for MoS_x. More importantly, optimization of the morphology of the PLD-grown TMDs enables a very efficient operation at high current density and in device-comparable conditions, with a particular attention on the optimized MoS_x which exhibits a remarkable 120 hour stability at -100 mA cm^{-2} and a 25 hour stability at -1 A cm^{-2}, an unprecedented result for non-crystalline TMDs.

The results of this work show how a catalyst design strategy that controls the material over multiple length scales endows non-metallic, alternative electrocatalysts like TMDs with both high intrinsic activity and efficiency operation at high current, representing an important step in the implementation of these materials in operative devices and in pushing the performance threshold of TMDs closer to the state-of-art metallic benchmarks.

MAINTENANCE MANAGEMENT BY CONDITION-BASED PRA WITH VOI-BASED OPTIMAL CONDITION MONITORING AND DATA ACQUISITION

Seyed Mojtaba Hoseyni - Supervisors: Francesco Di Maio, Enrico Zio

In the last few decades, the increase of energy demand has not been followed at the same pace by the installation of new energy generation facilities. As a result, the aging worldwide fleet of energy generation facilities will be capable of addressing the demand only if their life is extended. Digitization brings new opportunities for evaluating the viability of life extension and monitoring its effects on reliability and safety, thanks to the intelligent sensoring of Systems, Structures and Components (SSCs) through which monitoring data can be collected and used within risk assessment models to take risk-informed maintenance decisions that enable life extension. In this context, the objective of the PhD thesis is to develop a computational framework for condition-based risk-informed decision-making, which includes: I. Value of Information (VoI)-based data acquisition, and II. Condition-Based Probabilistic Risk Assessment (CB-PRA) maintenance decision support. Regarding I, a novel computational approach is introduced to identify the optimal positioning of sensors for condition monitoring of SSCs by VoI. VoI is a utility-based Figure of Merit (FoM), which quantifies the benefits of acquiring information for supporting the maintenance decision-making in a way to guarantee, at the same time, low cost, and valuable information. The VoI-based optimal sensors positioning is achieved by solving an optimization problem that maximizes the VoI among different sets of measurements using three different proposed optimization approaches namely, greedy, non-greedy and Subset Simulation (SS).
In terms of original contributions, the proposed advanced computational framework provides a simulation-based scheme for optimal condition monitoring and data acquisition for maintenance management and decision-making, as well as an innovative approach for developing condition monitoring guidelines, which have been traditionally relying only on operational experience.
With respect to II, an innovative framework is presented which makes use of the optimal condition monitoring data (obtained from I) within an innovative risk assessment framework (i.e., CB-PRA), for prioritizing the risk imposed on SSCs by different degradation mechanisms and taking the most proper decisions on the maintenance strategy to be adopted to control the degradation progression. This allows a proactive lifecycle asset management by allowing the decision-makers to taking real-time decisions on the optimal maintenance strategy for preventing accidents and balancing the maintenance budget expenditure.
The proposed framework of I is applied on a case study regarding the optimal sensors positioning on a Steam Generator (SG) of a Nuclear Power Plant (NPP) that is degrading under creep. Also, a SG Tube Rupture (SGTR) accidental scenario due to multiple degradation mechanisms is considered, to show the benefits gained by applying the framework in II.

A MULTI-LAYER ENERGY MODELLING METHODOLOGY TO SUPPORT HEAT-ELECTRICITY INTEGRATED DECARBONISATION

Francesco Lombardi - Supervisor: Emanuela Colombo

The decarbonisation of energy systems is urgent. Increasingly, the large-scale expansion of renewable capacity, combined with the electrification of the transport, heating and industry sectors, are seen as key to achieve such an ambition. In particular, coupling residential heating and power generation through power-to-heat technologies is raising increasing attention, due to their untapped potential to improve heating efficiency, power system flexibility and renewables penetration at once. However, the effects that the mass-scale electrification of residential heating would have on the electricity demand, on power system capacity expansion needs and on the supply-chain of other sectors are yet to be fully quantified. Energy system models are typically adopted to shed lights on such questions. Yet, the complexity of such problems, encompassing technical, economic, environmental and social dimensions, and involving a multitude of diverse stakeholders, unveils limitations in state-of-the-art models which require conceptual and methodological advancements. This thesis proposes a novel methodological conceptualisation of energy modelling, specifically conceived to go beyond such limitations. Energy modelling questions should be tackled from multiple perspectives, or layers. The energy system representation should be only one of such layers, to be systematically integrated with: the generation of demand profiles; the assessment of the impact of energy policies beyond the energy sector; and the mathematical control of the structural uncertainty arising from the identification of a single, optimal solution. I call this a multi-layer energy modelling methodology, whose conceptual structure is summarised in Figure 1.

More precisely, the idea is to have a first layer devoted to the generation of demand profiles for different heat end uses, with a regional (NUTS2 or higher) spatial resolution that allows to capture spatial differences in heat demand due to region-specific weather patterns. Second, to have a spatially-explicit energy system optimisation model with similar resolution, which allows to correlate region-specific heat demand profiles with accurate representations of regional P2H aggregate operational behaviour and renewable generation. Unlike common practice, such energy system modelling layer would not identify a single optimal capacity expansion strategy to meet the electrified heat demand profiles, but rather a set of near-optimal solutions, all equally feasible and close to the mathematically optimum cost. Third and final, to have an industrial-ecology modelling framework that, for each generated feasible capacity expansion strategy, computes the associated socio-environmental impact beyond the energy system domain.

My thesis demonstrates the advantages of such a multi-layer energy modelling methodology for a demonstrative case study, while also providing original scientific contributions pertaining to individual modelling layers, particularly as regards the generation of near-optimal solutions. To this regard, the thesis discusses the development of an original 'SPORES' algorithm, which goes beyond existing methods for the generation of alternatives inasmuch as it allows specifically to identify spatially distinctive ways of locating new energy generation capacity, such as for instance alternative and more socially acceptable ways of locating large wind farms.

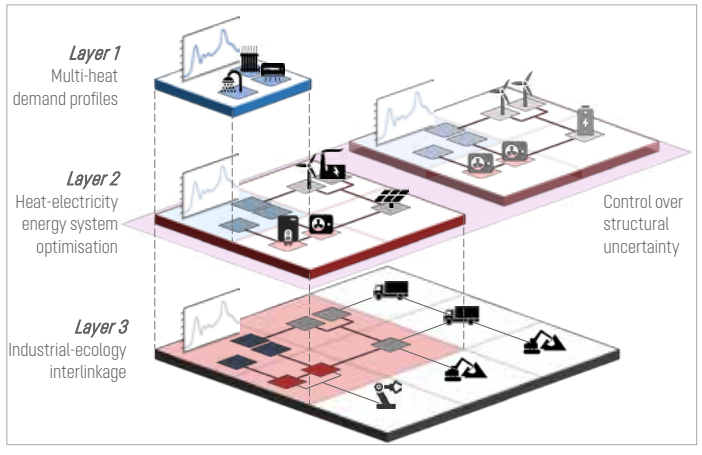

Fig. 1 - Conceptual scheme of the multi-layer energy modelling methodology

The application of the overall multi-layer workflow to Italy shows that heat-electricity integration is a no-regret option when efficiency and flexibility improvements are substantial, as for power-to-heat systems for domestic hot water. Otherwise, it requires integration within a broader renewable capacity expansion plan. To this regard, while results show that the rate of renewable capacity deployment required to sustain a large electrification of all energy sectors in Italy would be comparable with deployment rates recorded in years of high governmental support, deployment rates recorded in latest years are much lower. It is hence imperative to raise deployment rates, possibly taking advantage of the demonstrated flexibility for decisions like where to locate renewable, transmission and storage capacity, in such a way to maximise social and political acceptance. At the same time, the overall extent to which renewable capacity would need to expand could be mitigated by parallel policies aimed at achieving large demand reductions in sectors which showcase potential for doing so. For instance, the thesis results highlight how massive reductions in space heating demand could be achieved in Italy by means of building refurbishment policies targeting older buildings. In summary, and with particular reference to heat-electricity integration in Italy and beyond, the insights from this thesis suggest that it is critical to combine: i) the mass-scale deployment of no-regret power-to-heat systems, such as those tailored to domestic hot water supply; ii) country-wide building refurbishment policies; and iii) strategies for the expansion of renewable capacity that ensure deployment rates in line with those achieved in peak renewable deployment years, building on the demonstrated flexibility in decisions like where to locate capacity.

Overall, the multi-layer energy modelling methodology can support policy making in the context of the renewable energy transition and its associated sectoral integration, even beyond the specific problem of heat-electricity integration. Yet, it has scope for further enhancement. The results of the thesis highlight that it would be particularly important to improve the ways by which weather and climate uncertainty are accounted for in energy models, in such a way to generate feasible energy infrastructure deployment options which are simultaneously robust with respect to a wide range of weather conditions, including particularly unfavourable ones.

RISK-INFORMED OPTIMIZATION OF MITIGATION STRATEGIES IN SAFETY-CRITICAL SYSTEMS

Alessandro Mancuso - Supervisors: Ahti Salo, Enrico Zio

Co-supervisor: Michele Compare

Industrial organizations need to invest in the design and operations of their production systems to improve reliability, availability, maintenability and safety. Typically, these organizations have limited resources, therefore they can select only a subset of mitigation actions to protect the system from the risks associated with accident and threat scenarios. For this reason, optimization models for resource allocation are necessary to minimize the risks of such scenarios.

In current practices, resources are often allocated based on the failure risk of the individual components, which can lead to sub-optimal solutions. By contrast, this Dissertation proposes systemic analyses of accident and threat scenarios in order to determine the optimal mitigation strategy for the overall system. The optimal strategy is a combination (portfolio) of mitigation actions for system design and operations that minimize the systemic risks, while satisfying relevant budgetary and technical constraints.

For this purpose, the probabilistic analysis of the systemic risks is performed through Bayesian models to capture the uncertainties of the accident and threat scenarios. Then, the selection of the optimal resource allocation builds on Portfolio Decision Analysis to determine the optimal portfolios consisting of a set of discrete alternatives. In addition, the methodologies allow a range of sensitivity analyses on budget allocation and risk management of the accident and threat scenarios.

The methodologies are illustrated by revisiting real-life case studies and reported examples in the context of system design and operations, to demonstrate that systemic analyses can outperform the current practices on component-based resource allocation. The methodologies are also generic in that they can be employed in other application areas with reasonable adaptations.

PLASMA ENHANCED CATALYTIC REMEDIATION OF METHANE RESIDUALS IN THE AFTER-TREATMENT SYSTEM

Matteo Molteni - Supervisor: Alessandro Donazzi

The greenhouse gasses emissions reduction is gaining an increasing interest in the past years. Whether or not they are related to the world average temperature inacrease, the anthropogenic emissions are steadily increasing, especially the ones generated by the transportation sector. Methane is a greenhouse gas with a global warming potential around 25 times higher than carbon dioxide and considering that it constitutes a valid alternative to traditional fuels (such as gasoline), it could play a significant role in the fuels market in the future. The combustion process not always leads to a complete combustion of the reactants, and therefore methane emission has to be accounted for in the after-treatment system.

An experimental and a modelling analysis of a non-thermal plasma reactor for the abatement of methane emissions is presented. The system studied consists of a catalytic packed-bed reactor with a plasma stage applied to it. Two configurations are considered: in a one-stage reactor the plasma is generated within the catalytic bed, while in the two-stages configuration the plasma region is placed before the catalyst. Two models are coded to deal with respectively the gas phase plasma reactions and the surface catalytic ones.

The first modelling approach presented describes the gas-phase plasma chemistry, and the model includes mass balances for neutral, charged and radical species, the enthalpy balance for the gas phase and specific equations for electron temperature and density. The kinetic scheme of methane abatement couples the GRI-Mech set of radical reactions (325 steps) with ten sets of plasma reactions (108 steps), which comprise elastic collisions, direct ionization, dissociative ionization, excitation and attachment reactions. The model is validated based on literature results that explore the effects of Specific Input Energy, gas temperature and water vapour addition. The results highlight that dissociative electron-impact reactions produce chemically active OH and O radicals, which boost CH_4 conversion, making H_2O a key abatement promoter in the plasma process. The heating effect induced by electron collisions is relevant, suggesting that an accurate control of thermal insulation is crucial to characterize the reactor performance.

The catalytic-surface reactions are modelled with a mono-dimensional time dependent approach. The species evolution in both the gas and solid phases is described with mass and energy balances. The packed bed properties (i.e. the mass diffusion coefficients and the heat transfer rate) are estimated with literature correlations and the use of the j-factors and the Chilton-Colburn analogy. The model allows to investigate the catalytic activity towards the relevant surface reactions involved in the methane abatement process, such as the methane and carbon monoxide surface oxidation.

An experimental analysis on the parameters affecting the methane abatement process in a dielectric barrier discharge reactor is presented. Methane is converted at atmospheric pressure with large excess of oxygen and with argon as a diluent. The temperature is controlled with a custom quartz chamber and an air blower. A catalytic material 5% Pd/Al_2O_3 is used in conjunction with the plasma process, adopting three reactor configurations: empty reactor (plasma only), one stage and two stages. The effects of the operative temperature and the plasma specific input energy on methane conversion and are first analysed. The impact of the feeding gas composition is also examined through the introduction of carbon dioxide amongst the reactants and replacing the diluent gas with nitrogen. Lastly, a comparison from an energetic standpoint between the catalytic and the plasma processes is presented. The results highlight that the plasma process converts CH_4 mainly in CO. The presence of a catalytic material becomes then crucial to complete the oxidation process. The analysis also shows that the gap between thermal catalysis and plasma is still large in term of energy requirements, and further improvements are needed to make the plasma technology competitive for emission control processes.

CFD MODELING AND VALIDATION OF SPRAY EVOLUTION IN GASOLINE DIRECT INJECTION ENGINES

Davide Paredi - Supervisor: Tommaso Lucchini

The present work focuses on the numerical characterization of the gasoline direct injection process performed in modern spark-ignition engines for vehicle applications. A detailed prediction of injection and air–fuel mixing is in fact a mandatory task to guarantee a stable and efficient combustion process with the aim to minimize pollutant formation. Within this context, computational fluid dynamics simulations represent a powerful tool to assess the main physical phenomena related to breakup and evaporation of the liquid jet, leading to mixture formation by means of the interaction between the vaporized fuel and the charge motion. To ensure the accuracy of the computed results, so that they could be a reliable support for industrial design and research activities, it is mandatory to validate the adopted multidimensional spray sub-models against available experimental data under well-defined operating conditions. To this end, the multi-hole gasoline direct injection Spray G injector made available by the Engine Combustion Network community was chosen as the reference geometry for the validation of the proposed numerical setup. Simulations were carried out with the open source OpenFOAM software coupled with the LibICE framework which consists into a set of libraries and solvers developed by the Internal Combustion Engine Group of Politecnico di Milano and dedicated to the modeling of the most important physical phenomena related to internal combustion engines. In this work, at first a reference numerical spray setup was employed and tested under a wide range of Spray G operating conditions. By validating the results in terms of axial spray penetration, gas velocity, entrainment, spray morphology and Sauter Mean Diameter it was possible to observe strengths and weaknesses of the approach and thus propose specific improvements. An innovative liquid post-processing procedure, developed for the ECN6 Workshop and based on a projected liquid volume Eulerian field, represented the reference validation methodology for the proposed numerical improvements of atomization and secondary breakup which were implemented into the LibICE framework. More in detail, two solutions based on a decoupled approach for the management of primary and secondary atomization under a single spray model were proposed and validated in the present work. Furthermore, a literature-based evolution of a classic secondary breakup model was considered and implemented into the LibICE with the aim to provide a dynamic approach for droplet stripping and catastrophic breakup which could better suit the low-evaporating conditions of early injection events typical of modern gasoline direct injection engines. Two literature-based flash boiling evaporations models were implemented as well and validated on a dedicated Spray G flashing operating condition. The proposed numerical setups were also reproduced under dynamic conditions by performing simulations of a full-cycle of two modern gasoline direct injection optical access engines, one of which was directly coupled to the Spray G injector. Finally, the physical phenomenon of collision between liquid drops during the injection process has been studied by implementing into the LibICE framework a literature model whose main purpose was to reduce the required computational time compared to other available mechanisms. The validation of the model was carried out by running different Spray G simulations and by comparing computed axial vapor penetration and droplet diameter with those calculated without collision and with other dedicated models already available in OpenFOAM. On the basis of the observed results a further model modification was then proposed with the aim to achieve a better compromise between numerical accuracy and minimization of the required computational time.

FABRICATION AND CHARACTERIZATION OF CARBON-ATOM WIRES AND WIRE-BASED NANOCOMPOSITES

Sonia Peggiani - Supervisor: Carlo S. Casari

In last years, the investigation of the third allotrope of carbon based on sp hybridization, the so-called carbyne, has revealed extraordinary theoretically predicted properties. The structure-dependent optoelectronic properties, the huge effective area (~3000 m^2/g), the high Young modulus (~32 TPa), the high electron mobility (1.5 x 10^5 cm/V·s) and the high thermal conductivity (148 kW/m·K) are only some examples of the outstanding properties of carbyne. Those results raised up the interest of the scientific community on finite sp-carbon chains and their possible applications in different fields. These structures, also called carbon-atoms wires (CAWs), exist in two different configurations, one with alternated single and triple bonds (i.e. polyyne), and the other one with a sequence of double bonds (i.e. cumulene). They are naturally synthesized in interstellar and circumstellar medium. In addition, CAWs can be indeed employed as active materials in electronic devices, for live-cell imaging, optical barcoding and as materials for energy applications (e.g. photovoltaic, water splitting, hydrogen storage media). The major issue of sp-carbon chains concerns their poor stability under ambient conditions because they tend to spontaneously rearrange in more stable sp^2 structures.

In this work, first, the synthesis and characterization of polyynes at single wire level were performed and then, the preparation and study of properties of wires-based nanocomposites were carried out. CAWs-based materials respond to a two-fold aim: stabilizing sp-carbon chains and being applied in different technological fields.
With this last-mentioned aim, it is important to exploit synthesis techniques that are cost-effective and scalable for a possible future mass production. From this perspective, physical methods as submerged arc discharge in liquid (SADL) and pulsed laser ablation in liquid (PLAL) were employed in this thesis.

Water was first selected as a solvent for SADL and PLAL due to its low cost and for possible environment-friendly applications and need a further investigation because it has been reported only in few works of literature. Since water cannot contribute as carbon source during CAWs formation, the yield of polyynes in water is lower with regard to organic solvents, so the synthesis parameters were optimized, and post-synthesis concentration methods were also involved. In this regard, a novel procedure to automatize the concentration, separation, and collection of size-selected polyynes in water was developed during this thesis.

With the intention of studying polyynes evolution during arc discharge, *in situ* surface-enhanced Raman spectroscopy (SERS) measurements were conducted for 40 minutes during arc discharge in aqueous solution with Ag nanoparticles previously made by SADL.

In addition, organic solvents, as acetonitrile and isopropanol, mixed with distilled water were employed in SADL, producing hydrogen-, methyl- and cyano- capped polyynes of different length. In the case of PLAL, pure organic solvents, i.e. acetonitrile, methanol, ethanol and isopropanol, were utilized. In this way, the effect of different solvents during PLAL experiments on polyynes properties, e.g. size, termination, yield and stability, was studied by a multi-technique characterization. An extended range of CAWs were individuated and separated. Since some of the species were not already reported in literature, all these outcomes were supported by time-dependent density functional theory simulations. Then, the differences revealed in SERS spectra bands of selected polyynes with 8 atoms of carbon capped by hydrogen, methyl- and cyano- group, respectively, confirmed the correct identification of these species. Moreover, the SERS sensitivity to terminations was thus demonstrated. Some considerations on the mechanism of formation of polyynes in liquid emerge from the discussion of the obtained results. First, solvents during ablation/arc discharge can contribute to the formation of sp carbon chains by giving carbon, hydrogen atoms or entire functional groups, as cyano- or methyl- group, depending on the solvent molecular structure. Second, the identification of HCnCH3 in water, whose structure is not characterized by methyl-groups, can be due to the binding of three hydrogen together with a carbon atom produced during the synthesis process. To study the stability of polyynes solutions, different conditions were experimented. The exposure to air decomposes CAWs more quickly than the exposure to solar light and to temperature of 323.5 K. In fact, polyynes dried on a silicon substrate degrade immediately unless Ag colloids are added to the solution before the solvent evaporation. In this way, silver nanoparticles, strongly interacting with polyynes, may change the electronic configuration or act as spacers by keeping distant the chains, so stabilizing CAWs at least for one month. Furthermore, it was observed that longer cyano-capped polyynes are less stable than shorter hydrogen- and methyl-capped species. Among the solvents selected in this study, acetonitrile is the one which preserves better CAWs. Consequently, it turns out to be the best solvent compared to water, methanol, ethanol and isopropanol, not only in terms of stability but also for polyynes yield and for the different types of chains that can be synthesized.

After the investigation of CAWs at single wire level, the preparation and characterization of polyynesbased materials were performed. A novel synthesis method, which consists of ablating graphite in a polymeric solution, allows the formation of polyynes *in situ*, directly in the polymer, so avoiding the heating or the dilution step of polyynes solution. This method was so far applied to two different polymers, i.e. poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA), and Ag nanoparticles necessary for structural SERS analysis can either be added to the solution in the form of chemically synthesized Ag colloids (in the case of PVA experiments) or be synthesized by irradiating a silver pellet in the polymeric solution before the ablation of graphite (in the case of PMMA experimental work). It was found that a good blending between polyynes, Ag nanoparticles and PVA was achieved at low concentration of PVA in water, i.e. of around wt. 1%, and the signal of the encapsulated hydrogen-capped polyynes was detected up to at least 11 months. Concerning PMMA/Ag/nanocomposites, stability of sp-carbon chains has been tested for 5 months. After the concentration of Ag nanoparticles, *in situ* SERS measurements were performed to study the evolution of the sp-signal during the synthesis by laser ablation of graphite in PMMA solution with Ag nanoparticles. The resizing and reshaping of Ag nanoparticles induced by laser ablation may justify the changes in position of the Ag nanoparticles plasmonic peak and consequently the different absorption at the Raman wavelength.

The results of this thesis pave the way to several further investigations, currently mainly oriented to stabilize and concentrate sp-carbon chains. The first aim can be achieved either by ending the single wires with a bulky group during the synthesis or by finding other polymeric matrices to encapsulate unstable wires, e.g. hydrogen-capped polyynes. The improved stability observed when polyynes are immobilized in PVA and PMMA matrices and the simplicity of the synthesis method here developed are significant steps for the preparation of new CAWS-based materials. The second point to address is to reach a polyynes concentration in nanocomposites capable of improving the polymer properties by the outstanding characteristics of carbon-atom wires. Another potential follow-up of this research could involve the study of oriented CAWs in free-standing films, and mechanical and electrical measurements on the nanocomposites in view of future industrial applications.

MODELLING OF CRITICAL COMPONENTS IN SOLAR TOWER PLANTS FOR DEGRADATION ASSESSMENT AND MAINTENANCE PLANNING

Giovanni Picotti - Supervisor: Giampaolo Manzolini

The challenges and the uncertainties that *climate change* is exposing mankind to are growing and worsening with a worrying rate in the last decades. Reliable and efficient renewable sources are required to guarantee a cleaner and sustainable energy supply for the whole planet. Concentrated Solar Power (CSP) plants are a promising technology that offers advantages like dispatchability and grid ancillary services, but is currently more expensive than competing technologies and thus require improvements to lower its cost of electricity. Within CSP, Solar Tower (ST) plants can achieve higher temperatures and hence efficiencies, which enable better performance.
The aim of this thesis is to study critical and unique key degradation modes that hinder the performance of ST plants and develop strategies to address them. Particular attention is given to the soiling of heliostats and the high-temperature-induced issues (corrosion, creep-fatigue cycles, absorptance reduction) of the central receiver.
The soiling process is modelled through a physical model developed and implemented using Matlab®. Three difference phases are identified to describe the deposition of dust particles from being entrained in air to their settling on the solar reflectors' surface: deposition, adhesion, and removal. The first phase calculates the so-called *deposition velocity* that expresses the speed at which dust particles settle vertically onto the heliostats' surface, while the second and third ones compute the balance between adhesion (van der Walls) and removal (gravity) forces. Eventually, the reduction of reflectance is evaluated with a geometrical model that computes the shading and blocking effect of dust particles deposited onto their surface. A *soiling factor* is finally defined that represents the reduction of reflectance of the heliostats.

$$f_{soil} = 1 - \frac{A_{soil}\left(\frac{1+sin\theta}{cos\theta}\right)}{A_{mir}}$$

Where A_{soil} is the total projected area of the deposited dust particles, A_{mir} is the reflective area of the heliostat, and θ is the incidence angle. The model is validated using experimental outdoor data recorded at the Queensland University of Technology (Brisbane, Australia) and further verified through indoor data collected at the Fraunhofer ISE (Freiburg, Germany).
The reflectance losses predictions are exploited to evaluate their impact on the generation and economic performance of a hypothetical plant deployed in Woomera (South Australia). A Mixed Integer Linear Programming (MILP) model is developed to perform the optimization of the cleaning schedule of the Solar Field (SF) of the plant, balancing the costs incurred due to cleaning and the revenues lost due to soiling. The outcomes of the MILP model include the best provisioning of cleaning resources for the whole plant and the timing of the cleaning of each sector of the SF, as depicted in Figure 1.

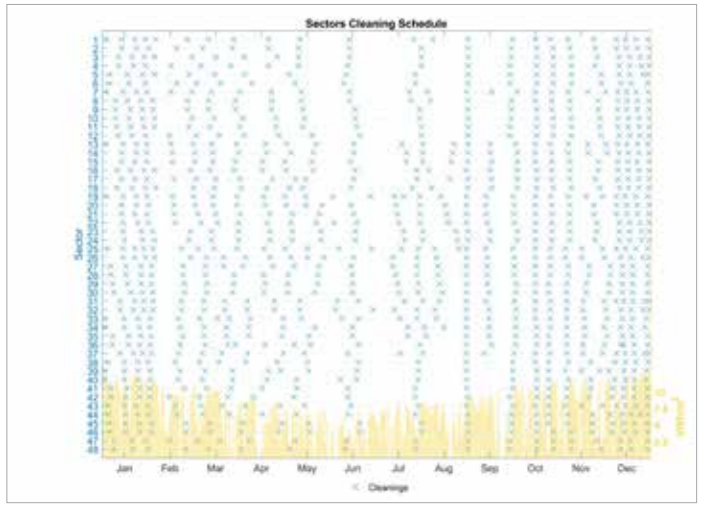

Fig. 1 - Cleaning Schedule Optimization

The analysis of the thermal behavior of the central receiver is realized using the open-source language Modelica® and the commercial software Dymola® through the application of the Object-Oriented Modelling (OOM) paradigm. The receiver is analyzed considering separately each panel, which is characterized by one representative tube. The tubes are discretized in the axial direction (1D model) and in both the axial and circumferential direction (2D model). A solar flux map that represents the radiative power reflected by the heliostats towards the receiver is coherently applied on the elements of the tubes. Much higher temperatures are obtained with the 2D model, since the 1D model ignores the circumferential flux variation and hence underestimates the maximum temperature achieved at the crown of the tubes. Radiative losses towards the environment are computed through equivalent thermal resistances that include ad - hoc assessment of the view factors. Heat transfer correlations are exploited to calculate the natural and forced convective losses, and the heat absorbed by the Heat Transfer Fluid (HTF) and its consequent variation of enthalpy (and hence temperature). Inertial terms are considered for both the tubes and the HTF to properly assess the dynamics of the system. Eventually, a PI controller is added to the system to set the desired outlet HTF temperature throughout the day and in the event of clouds. A cloudy day behavior is depicted in Figure 2. The developed model allows to assess the coating absorptance reduction and metal corrosion due to high temperatures, and to evaluate the impact of soiling on the receiver's tubes temperature. Eventually, the detailed knowledge of the temperature of the tubes provides valuable information for tools designed to predict degradation phenomena, ruptures, and thermal stresses, hence reducing efficiency losses and risk of failures.

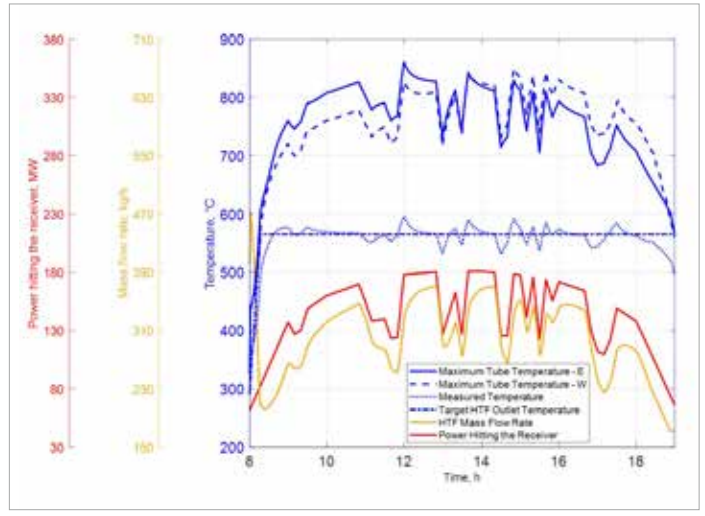

Fig. 2 - Receiver Dynamic Simulation

To summarize, this thesis deals with the identification, the modelling, and the mitigation of the detrimental effects induced by the degradation modes that affect the main and most solar-specific components of a ST plant: the solar field and the central receiver. The developed physical-based models are applied to predict the extent of the induced generation losses and to assess the impact of each degradation mode on the overall performance. Eventually, strategies for mitigation of the performance hindering effects are developed and presented.

NUMERICAL AND EXPERIMENTAL STUDIES OF PLASMA-MATERIAL INTERACTION IN LINEAR PLASMA DEVICES

Michele Sala - Supervisors: Matteo Passoni, Andrea Uccello

Introduction and motivations

Magnetic Nuclear Fusion aims to confine a hot mixture of light gases in the plasma state using strong magnetic fields, shaped in toroidal arrangement. The best example of this strategy is the tokamak one. The confinement provided by the magnetic field in a tokamak device is not perfect. Indeed, as a consequence of turbulence-related phenomena, particle as well as energy leaks from the confinement region leading to an unavoidable touch between the hot plasma and the vessel of the machine. The interaction between plasmas and materials goes under the name of Plasma-Material Interaction (PMI) and it is one of the most important topic in the field of Magnetic Nuclear Fusion. The reasons are due to the complex and interrelated phenomena typical of PMI. Due do this, materials to be used for the vessel wall facing the plasma (the so-called first-wall, FW) are of crucial importance. For its favourable thermophysical properties, tungsten (W) has gained a growing attention for the most critical component of the FW. Indeed, W has been chosen as the reference material for the most critical components of the ITER tokamak. The high particle and energy loads to which W is exposed can lead, however, to unavoidable modifications of W at the micro/nano-scale. Since, present-day tokamak experiments cannot reach the operative conditions foreseen in ITER, the behaviour of W cannot be fully addressed and a complementary numerical and experimental approach is needed. Numerical codes aim, from one side, to predict the plasma parameters in the outermost region of the tokamak, the edge plasma. From the other, they provide insight on how materials are eroded and transported into the plasma. Tokamaks are intrinsically complex devices and plasma conditions between discharges change. Therefore, is quite difficult to pinpoint a material modifications to a given plasma parameter. Thus, to address PMI in ITER-relevant conditions one needs a complementary strategy. Linear Plasma Devices (LPDs) are simple and cost-effective machines which can help to shed light on PMI. From the experimental point of view, LPDs thus allow for a lab-scale approach to PMI, which would be otherwise difficult. In parallel to this experimental investigations, it is also of great importance to use numerical codes also for plasma and materials modelling in LPDs. Indeed, in spite of their importance for PMI studies, only a scarce attention has been paid to the applications of modelling tools, commonly employed to tokamaks, also to LPDs. This application is of great relevance, since it allows from one side to test codes in simpler geometry and, from the other, also to interpret experiments.

Goals

My Ph.D. activities fall in the framework outlined above. In particular, I focused on the numerical and experimental investigations of PMI in linear plasma devices, using the GyM linear machine of ISTP-CNR. The numerical activities focused on the adaptation and application of the edge plasma code SOLPS (specifically, its most recent version SOLPS-ITER) to the GyM device and, in general, to LPDs. The material side of PMI is numerically investigated through the ERO2.0 code. The experimental activities focus instead on the production, via material science techniques (mostly using the Pulsed Laser Deposition technique), of W samples, having different morphology, structure, composition and roughness with respect to that of conventional bulk W. These samples are then exposed to fusion-relevant plasma here GyM LPD facility.

Results

SOLPS-ITER modelling of Ar plasmas in the LPD GyM

Simulations of GyM Ar plasmas have been performed with SOLPS-ITER. We performed a detailed sensitivity scan on the code free parameters, focusing on the variation of the diffusion coefficients, the overall absorbed electron power and the neutrals (i.e. Ar atoms) pumping efficiency. The results of this sensitivity scan have been interpreted both qualitatively and quantitatively. The qualitative analysis of the sensitivity scan was further reinforced by a comparison with experimentally-measured radial profiles in GyM, showing a good qualitative qualitative and quantitative agreement. The quantitative analysis of the sensitivity scan have been performed by considering the global particle and energy balance. This analysis allowed to better understand which terms are the most relevant in determining the plasma profiles in GyM. It has emerged that the main sources and sinks terms are related to the interaction with neutral particles

ERO2.0 modelling of nanoscale morphology evolution

The ERO2.0 morphology evolution capabilities have been put in perspectives with well-established models for surface morphology evolution, proposed in the field of semiconductors and material science. Among these, the Skeren model (SM) describe the evolution of the surface morphology as due to two phenomena: i) the dependence of the sputtering yield on the incidence angle and ii) the dependence of the sputtering yield on the crystalline grain orientation. In addition to these erosive surface mechanisms, in the SM also, iii), a surface smoothing contribution (proportional to the biharmonic operator) is added to account for adatoms diffusion. Through this analysis, it emerged that the SM is similar to the model currently implemented in ERO2.0, with the exceptions of ii) and iii). To make the comparison more quantitative, I implemented the SM in FreeFem++ (FM) and focused on the comparison of the FM and ERO2.0, using both simple morphology as well as realistic ones derived from dedicated AFM measurements. In general, a satisfactory agreement between the FM and ERO2.0 have been observed. A comparison of the simulations results between the realistic surfaces and dedicated experiments carried on during my Ph.D. pointed to discrepancies, related to limitation in the current physics contained in ERO2.0.

Exposures of W-based coatings to fusion-relevant plasmas in GyM

Part of my Ph.D. activities dealt with experimental investigations in the PMI field. I focused on the production and exposures of W-based coatings to fusion-relevant plasmas in the LPD GyM of ISTP-CNR. These W coatings were produced with the PLD apparatus available at NanoLab. Once deposited, a selection of these coatings have been exposed to fusion-relevant plasmas D and He plasmas in the GyM devices, under different irradiation conditions. We observed important modifications at the nano (formation of nanostructures) and microscale (formation of blisters). These modifications have been thoroughly investigated and compared with literature results. In this way, it was possible to better understand the mechanism behind the formation of the induced modifications.

Conclusions

This Ph.D. work dealt with the investigation of PMI in LPDs, adopting a combined numerical and experimental strategy. Having briefly summarised in the previous section the main results of this Ph.D. work, we can say that, as regards the numerical objectives:

- SOLPS-ITER has been successfully applied for the first time for the modelling of Ar plasmas in the GyM device, showing a good qualitative and quantitative agreement with measured parameters.
- A careful comparison of the SM and ERO2.0 on simple, analytically-defined surfaces, and realistic W surfaces retrieved from experiments showed a satisfactory agreements. However, a comparison of the SM and ERO2.0 with experimentally-available data revealed discrepancies which point to deficiencies in both models.

As regards the experimental aims:

- The exposures of W samples in GyM D and He plasmas revealed several modifications at the nano and micro-scale. This modifications were also previously reported in literature, but here they were observed in a rather new plasma regimes, in terms of ion energy and particle fluxes. This exposures allowed me to further extend literature results regarding possible explanation for their formation.

THERMODYNAMIC OPTIMIZATION OF THE ALLAM CYCLE AND THERMO-FLUID DYNAMIC DESIGN OF THE COOLED CO_2 TURBINE

Roberto Scaccabarozzi - Supervisors: Emanuele Martelli, Manuele Gatti

Co-supervisors: Stefano Consonni, Paolo Chiesa

This Ph.D. thesis aims at performing an in-depth analysis of the Allam cycle technology and related challenges, pursuing the following goals: (i) assess the maximum achievable efficiency and the optimal operating conditions of the cycle, improve the cycle model, and perform a more rigorous analysis than the existing literature; (ii) evaluate the Allam cycle's operational flexibility by developing part-load control strategies and analyze their performance at different loads, starting from 90 % down to 20 %; (iii) develop a detailed 1-D cooled-expander model, generally valid also for other expander types; (iv) design, develop, and optimize an improved oxy-fuel cycle configuration featuring a Brayton cycle integration with a solid oxide fuel cell (SOFC).

Based on the detailed Aspen Plus model developed, the Allam cycle can achieve an optimal net electric efficiency of 55.2 % featuring a turbine inlet and outlet pressures of 28.4 MPa and 4.7 MPa, respectively, and a turbine inlet temperature of 1397 K. Differently from conventional gas cycles the Allam cycle reach maximum performance with relatively low turbine inlet temperature due to the significant penalization of increasing the cooling flow mass flow rate. Furthermore, a higher turbine inlet temperature increases the coolant temperature, and consequently its mass flow rate, due to the higher turbine outlet temperature and the greater heat available in the regenerator. It is possible to reduce the turbine inlet pressure down to 24 MPa without a significant efficiency penalization thanks to the regenerator's compensation effect, which allows reducing the net specific work while increasing the combustor inlet temperature. However, below 24 MPa, the change in thermodynamic properties at the cold side of the regenerator leads to a sub-optimal thermal integration, which quickly reduces the net cycle efficiency.

The systematic optimization, performed constraining the turbine outlet temperature and inlet pressure, to reduce the mechanical and thermal stress of the regenerator, has shown that several different configurations of the Allan cycle allow the maintenance of the net electric efficiency above 52 % even with less demanding component operating conditions. An attractive configuration features a turbine inlet pressure 30.7 MPa and a turbine outlet temperature of 998 K. The efficiency penalization is only 0.3 percentage points compared the optimal case. However, it features a higher net specific work (+67 kJ/kg, i.e. 24 % higher than the maximum efficiency cycle) while reducing the high-temperature section of the regenerator heat transfer area. The economic assessment of this cycle configuration has shown that the Allam cycle can achieve economic performance close to state-of-the-art technology for carbon capture from natural gas-fired power plants, represented by post-combustion capture technology based on a MEA absorption process. Even if the specific investment cost is higher for the Allam cycle, the high net electric efficiency and the ability to avoid any emission of carbon dioxide allow achieving electricity and CO_2 avoided costs only marginally (i.e. 8 % and 10 %) higher than the MEA capture system.

The analysis of the part-load control strategies for the Allam cycle has shown that reducing the minimum cycle pressure and partializing the turbine admission arc have positive effects on the part-load performance. However, the best control strategy depends on the load. When the load is above 60 %, the penalty produced by partializing the turbine is not justified, however, when the load decreases below 60 %, the high turbine inlet pressure, allowed by the partial admission, compensates its fluid-dynamic penalty and becomes advantageous. Furthermore, according to the study assumptions, using a partial admission turbine is the only way to reduce the load below 30 %, and further increase the plant flexibility. Compared to controlling only the compressor inlet and diffuser guide vanes, optimizing the control strategies gives considerable efficiency gains, especially when the load is below 40 %. Under the assumption that the air separation unit can be operated at reduced load without significant penalization and stable combustion can be achieved at low cycle loads, the Allam cycle achieves better cycle efficiency and turndown capacity than a conventional combined cycle.

The developed 1-D mean-line code to estimate the preliminary row-by-row geometrical aero-thermal design of cooled turbines has highlighted that, for the selected Allam cycle configuration, the sCO_2 turbine requires between 5 and 6 stages. When a higher number of stages is featured, the turbine efficiency is improved by 1 percentage point, but the obvious drawback is the higher investment cost of the machine. Adopting a non-uniform distribution of the load coefficient and reducing it throughout the expansion (front-loaded configuration) has a positive impact on the turbine efficiency due to the lower coolant requirement, which is derived from the faster temperature reduction of the working fluid. Thus, the repeating stage configuration, which is usually adopted in uncooled sCO_2 turbines, is not suited for the optimal design of cooled machines. Furthermore, to cope with the high increase of the working fluid's volumetric flow rate, increasing the flow coefficient could be beneficial for an optimal design. The simulation results have further confirmed that the film cooling technology is less effective than conventional gas turbines due to the higher Reynolds number of the flow in the blade channels. Finally, due to the lower turbine inlet temperature, the smaller metal surface of the first stages, and the higher heat capacity of cooling flows, compared to conventional gas turbines, the cooling flow requirement of the Allam cycle's sCO_2 turbine is significantly lower. It is worth point out that the chord length plays a key role on the assessment of the cooling flow requirement, however, in order to determine it value a detailed mechanical evaluation of the stress produced by the change in momentum of the working fluid, the centrifugal forces, and the thermal stress has to be carried out.

Another outstanding result is the efficiency of the hybrid fuel cell - semi-closed CO_2 cycle (named SOS-CO_2 cycle), reaching net electric efficiency of 75.7 % with 100 % CO_2 capture. The cycle can be designed to operate with supercritical conditions of the CO_2-rich working fluid, or with more conventional pressures (as low as 2.75 MPa), keeping an outstandingly high efficiency (in the range 73 ÷ 76 %). Similarly, the system can preserve a high efficiency also when using an uncooled turbine or a fuel cell with low fuel utilization factor. Finally, if the separated CO_2 stream is captured and stored, and the condensed water properly managed by a waste-water treatment unit, the proposed power plant has zero emissions of pollutants and CO_2. In case very high purity CO_2 is required by the CCS chain, a CO_2 purification unit is needed, and the only vent gas stream released by the plant (actually very limited in flow rate compared to the captured one) would be the off-gas from the CPU, which is expected to include mainly CO_2, water and O_2.

EXPERIMENTAL INVESTIGATION AND MODELLING OF THERMO-CHEMICAL AND THERMO-PHYSICAL PROPERTIES OF FLUORIDES FOR THE MOLTEN SALT FAST REACTOR

Alberto Tosolin - Supervisors: Lelio Luzzi, Ondrej Beneš

This PhD thesis deals with the investigation of thermo-chemical and thermo-physical properties of fluorides, giving a significant contribution to the development of the Molten Salt Fast Reactor (MSFR), a nuclear reactor concept currently under consideration by the Generation IV International Forum (GIF). The MSFR has: the nuclear fuel (Th, U and/or Pu in form of fluorides) dissolved in a matrix of lithium fluoride operating as coolant; a non-moderated neutron spectrum; and an innovative design. These features combined confer great potentialities in terms of safety and sustainability, and a consortium of European partners has been studying the MSFR to meet and verify these ambitious goals. The work described in this PhD thesis contributed to the Horizon2020 Project SAMOFAR (http://samofar.eu/), which ended in 2019. New efforts for developing the MSFR are currently coordinated in the framework of the Euratom Project named SAMOSAFER (https://samosafer.eu/).

The investigation of safety-related properties of the liquid fuel is a crucial issue and must be faced considering accuracy and uncertainty of the results. Numerous difficulties characterize the experimental approach, e.g.: the commercial unavailability of plutonium trifluoride (which must be synthetized in-house); the purity of the end-members (highly hygroscopic and sensitive to oxygen); the radioactivity of the samples (which implies working in glove boxes); the high melting temperatures of fluorides (significant source of uncertainty); the corrosiveness of fluoride vapours (which require encapsulation of the samples); and the liquid state (making thermal conductivity measurements very challenging).

Synthesis of actinide fluorides and measurements were personally carried out at the Joint Research Centre (JRC) in Karlsruhe, exploiting mobility programs in the framework of the FP7-GENTLE and the H2020-ENEN+ European Projects. Because of their strong connection with the safety of the MSFR, phase equilibria, heat capacity, vapour pressure and thermal conductivity were assessed by experimental methods and modelling. Each task involved different fluoride systems, according to the state of the art of the specific topic and considering the most useful next steps for the development of the MSFR.

More in detail, the following issues were faced:

- Synthesis of highly pure PuF_3 at a gram-scale;
- Measurement of phase equilibria temperatures of LiF-PuF_3 and ThF_4-PuF_3 systems, and calculation of phase diagrams (CALPHAD); Measurement of high temperature heat capacity of ThF_4 by drop calorimetry and differential scanning calorimetry (DSC);
- Vaporization behaviour of selected MSFR fuel mixtures and end-members by Knudsen effusion mass spectrometry (KEMS);
- Development and assessment of a novel technique for measuring high temperature thermal diffusivity of molten salts using a laser flash (LF) device.

PuF_4 was synthetized by hydrofluorination of PuO_2, previously obtained by reaction of plutonium nitrate with oxalic acid and subsequent calcination of the oxalates. PuF_4 was then reduced to PuF_3 by hydrogenation. ThF_4 and UF_4 were synthetized at the JRC with similar steps but excluding the final reduction reaction. All non-actinide fluorides used in this work were purchased by external suppliers.

PuF_3 was mixed with LiF and ThF_4 and approximately 30 different binary compositions were assessed by DSC, using an in-house encapsulation technique to avoid sample vaporization during the measurements. Some samples were measured by X-ray diffraction (XRD) to assess possible formation of compounds and solid solutions during the heating ramps by DSC. JRC thermodynamic database was re-visited to obtain best fit between experimental points and calculated phase equilibria by CALPHAD approach. As a result, novel data for the LiF-PuF_3 system and first experimental results for the ThF_4-PuF_3 system were obtained.

High temperature heat capacity of solid and liquid ThF4 was measured by DSC and drop calorimetry. Samples were encapsulated using a JRC in-house laser welding technique. Several tests and adjustments to the experimental set-ups of the calorimetry devices were implemented to improve the consistency of the results. As a result, high temperature heat capacity of ThF_4 was measured for the first time, and good agreement between the two independent techniques was achieved.

Vapour pressure of pure UF_4 and PuF_3 was measured by KEMS to complete the JRC database of actinide fluorides of interest for the MSFR. Experimental results were used to determine vaporization enthalpy according to the second and third law of thermodynamics. Novel data on UF_4 and PuF_3 ionization potentials by electron impact and PuF_3 melting point were additionally measured during the experiments. KEMS was also used to measure partial vapour pressures of two fuel mixtures selected for the MSFR in the framework of SAMOFAR Project: the LIF-ThF_4-UF_4 (77.5-20.0-2.5 mol%) and the LiF-ThF_4-UF_4-PuF_3 (77.5-6.6-12.3-3.6 mol%) fuel mixtures. Boiling points of these compositions were estimated by extrapolation of the total vapour pressure to 1 bar.

Thermodynamic calculations of partial vapour pressures, performed using the JRC database, gave quite good agreement with the experimental results, which highlighted the safety features of the MSFR (low vapour pressures and high boiling points).

Since a reliable technique to measure heat transfer properties of radioactive molten salts at high temperature was not available, an innovative method was explored to couple a LF device with encapsulated samples. A novel crucible was designed, and adjustments were successfully made to couple it with the JRC laser welding device. The mixture LiF-NaF-KF (46.5-11.5-42.0 mol%), called FLiNaK, was used for validation as some experimental results are available in literature. To monitor the material inside after the welding and to quote sensitive dimensions and thicknesses, X-ray and tomography techniques were used. A finite element model was made to interpret the experiments and for the evaluation of the heat losses. The measurements showed a good agreement with previous experimental works, confirming the potentiality of the novel technique, despite some repeatability issues due to the positioning of the mixture inside the capsule.

This PhD thesis collects a significant amount of novel results on fluoride systems of great interest for the MSFR: PuF_3 was successfully synthetized, and PuF_3-containing systems were assessed by DSC for phase equilibria and by KEMS for vapour pressure measurements; drop calorimetry and DSC were strongly improved to make them more reliable when encapsulated samples are used (the quality of the improvements was confirmed measuring for the first time the high temperature heat capacity of ThF_4); a novel technique for coupling encapsulated molten salt samples with a LF device was developed and validated at high temperature.

The work carried out paves the way for measuring other systems fundamental for the MSFR, e.g., phase equilibria of ternary systems containing PuF_3 and the heat capacity of this halide. KEMS measurements reported in this PhD thesis represent a benchmark when studying variations in fuel compositions (e.g., addition of fission products). Finally, the capsule for measuring thermal diffusivity of molten salts by LF, following the implementation of some adjustments to improve the repeatability, might represent a significant step forward in the measurement of heat transfer properties of molten salts for nuclear applications.

DEEP LEARNING AND RESERVOIR COMPUTING FOR PROGNOSTICS AND HEALTH MANAGEMENT WITH MISSING DATA AND INFORMATION

Mingjing Xu - Supervisors: Piero Baraldi, Enrico Zio

Co-supervisor: Sameer Al-Dahidi

Prognostics and Health Management (*PHM*) is a field of research and application aiming at detecting abnormal conditions in industrial systems, diagnosing their causes and the degradation level of the components and predicting their remaining useful life, with the objective of increasing the system safety, reliability and availability and reducing the cost of maintenance.
In the era of Internet of Things, the rapid growth of the amount of data collected during the operation of industrial systems makes possible the development of more accurate and efficient *PHM* methods based on the advantages of artificial intelligence.
However, the data typically available for PHM are characterized by:
1) the scarcity of signal measurements collected from industrial systems in abnormal conditions. This is due to the fact that faults are rare, especially for safety related systems;
2) the lack of information about the true system state in correspondence of the collected signal measurements; this depends on the large cost and intensive labor of domain experts needed for retrieving this information;
3) the lack of measurements continuously collected during the operation of the industrial systems. This is due to the fact that data are often collected at irregular time steps, e.g. in correspondence of the occurrence of triggering events at the system level, and to the difficulties of managing and storing the large amount of monitoring data.
In this context, the present PhD work develops a novel framework for PHM in case of missing information, which is one of the most limiting issues toward the real applications of prognostics and health management to industrial systems. The proposed framework is based on the use of Deep Learning (DL) and Reservoir Computing (RC). Deep Learning methods have been considered given their ability of learning the complex distributions of the data collected from industrial equipment, whereas RC methods allow capturing the long-term dynamics of the degradation and failure processes.
Specifically, with respect to *1)* a method for fault detection based on Generative Adversarial Networks (*GANs*), Auto Encoder (*AE*) and adaboost ensemble learning has been proposed. The main novelty is the development of an ensemble of Encoder-aided *GANs*, which is shown able to identify the boundary of the complex, high dimensional, non-smooth, manifold distributions of the healthy data. The proposed method has allowed improving the detection performance with respect to state of the art methods.
With respect to *2)*, a method based on Reservoir Computing *(RC)*, Conceptor and spectral clustering has been developed for degradation level classification. The novelty is the use of Conceptors for the extraction of degradation indicators. The obtained representation of the long-term degradation dynamics has allowed improving the diagnostic performance with respect to state of the art methods, which are typically limited by the use of sliding time windows of fixed lengths.
With respect to *3)*, a Remaining Useful Life *(RUL)* prediction model based on Echo State Networks (*ESNs*) and bagging ensemble has been developed. The novelties are the reconstruction of missing degradation information by updating the reservoir state without providing any input and the estimation of the uncertainty affecting the *RUL* predictions, which is obtained by using an ensemble of *ESNs*. The reconstruction of missing information in long-term degradation dynamics has allowed obtaining more precise RUL predictions than that obtained using state of the art prognostic methods.
The proposed framework is validated using data collected from electrolytic capacitors, equipment of high-speed trains and bearings used in different industrial areas.