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DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Coordinator:
Prof. Carlo Bottani

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

- production, conversion and transmission of energy
- rational use of energy
- nuclear systems, nuclear fuel cycle, radioprotection
- application of ionizing radiations
- methods for safety and reliability analysis
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EXPERIMENTAL AND NUMERICAL ANALYSIS OF MULTIPHASE FLOW WITHIN HORIZONTAL PIPELINE WITH VARIABLE CROSS-SECTIONAL AREA

Parham Babakhani Dehkordi - Supervisor: Prof. Luigi P.M. Colombo

The main purpose of this thesis is to study the hydrodynamic behavior of very viscous oil-water flow in ducts with variable cross-sectional area. Experimental investigation, theoretical modeling and CFD simulation approaches were conducted. Moreover, the last part of this thesis is devoted to very viscous oil-water-air flows in a horizontal straight tube.
Experimental results on very viscous oil-water flow through sudden contractions and expansions were discussed, reporting the main flow parameters such as distributed and concentrated pressure drop, flow pattern, and phase holdup. Three pipe configurations for sudden expansion (21-30 mm, 30-40 mm, and 30-50 mm) and one case for sudden contraction (30-21 mm) were selected. The main flow patterns included core-annular and dispersed flows. It was concluded that for the largest cross-sectional area change (30-50 mm), the dominant flow pattern is dispersed, whereas core-annular flow is the major flow pattern in the other configurations. The presence of sudden expansion caused the oil-water flow to be more eccentric. A mechanistic model based on the Two-Fluid Model (TFM) for fully-developed core-annular flow of oil-water mixtures was developed. A new correlation to compute water holdup as a function of measured pressure gradient, superficial water velocity, rheological properties of water was provided. Two differential pressure flow meters (VFM and NFM) have been developed to measure volumetric mixture flow rate. The mixture superficial velocity has been calculated generalizing Bernoulli's equation and introducing the definition of discharge coefficient from a suitably defined calibration curve.
Furthermore, CFD simulation of very viscous oil-water flow through measurement devices (VFM and NFM) as well as sudden expansion was studied by means of commercial CFD code Fluent, and the most important flow characteristics such as oil holdup, pressure gradients and flow patterns were predicted. Finally, it was shown that, CFD simulation was able to predict the core eccentricity without oil contact at the pipe wall during core-annular flow. This is consistent with flow visualization observed experimentally. The concentrated pressure drop through the convergent section of the VFM and NFM computed by CFD showed a very good agreement with experimental data.
The results of an experimental campaign devoted to three-phase flow of very viscous oil-water- air mixtures in a straight horizontal pipe (40 mm i.d.) were reported. Slug body, elongated bubble and total slug unit lengths were experimentally measured by optical probes. It was concluded that superficial gas velocity has a considerable effect on slug body and bubble length, that is, the higher the superficial gas velocity, the higher the slug body and bubble length.

THERMOMECHANICAL CHARACTERIZATION OF FUSION-RELEVANT NANOSTRUCTURED COATINGS

Edoardo Besozzi - Supervisor: Prof. Marco Beghi

The main goal of this Ph.D thesis is to provide, following an advanced laboratory scale materials science approach, a thermomechanical characterization of fusion-relevant nanostructured coatings to better clarify the role on such properties of the specific nanostructure, morphology and composition of the samples. It is well known that the thermomechanical properties of coatings can substantially differ from the ones of the corresponding bulk form, as these properties are hardly predictable. In this thesis, the target samples were chosen by considering coatings that mimic different coating scenarios found in operating tokamaks and expected for the future fusion reactor ITER. In particular, W coatings with different morphologies, from compact to porous, different structures, from nanocrystalline to amorphous, and different chemical compositions (i.e. W-tantalum, W-oxide and W-nitrides), and amorphous B coatings were deeply investigated. The coatings were de- posited, by Pulsed Laser Deposition, by other researchers of the Micro and Nano Structured Materials laboratory. In particular, nanocrystalline W coatings (c-W) were chosen as proxy of W coated plasma facing components of tokamaks (e.g. JET- ILW, ASDEX-UG, WEST). Amorphous and porous metallic W are, instead, considered as proxy of promptly redeposited W coatings, while W-oxide and W-nitride coatings as proxy of the results of co- deposition processes between W and gas impurities that can be found in the reactor. Finally, B coatings are also investigated for their relevance for the first wall conditioning of tokamaks. The analysis of these coatings was divided into three main tasks. In order to derive the thermomechanical properties of the samples, the first task of the thesis was the development of a novel experimental investigation method suitable for the thermomechanical characterization of coatings with a complex nanostructure. This method relies on the combined use of Brillouin spectroscopy, whose data analysis procedure was optimized to derive the elastic moduli of metallic coatings, and the substrate curvature method, exploited for the detection of thermal and residual stresses and the thermal expansion coefficient of various samples. An ad hoc experimental apparatus for the substrate curvature measurements was completely developed, tested and optimized during the three year Ph.D period. The coupling of this system with Brillouin spectroscopy turns out to be a powerful non-destructive and very versatile thermomechanical characterization method that was successfully exploited for all the above mentioned nanostructured samples.

Nanosecond laser irradiation was adopted for mimicking thermal effects, such as melting, cracking and crystallization, induced by ITER-relevant transient thermal loads. The use of nanosecond lasers for this type of fusion-relevant investigation was the first of its kind, therefore it was carefully validated. The validation was performed by a direct comparison between the thermal effects induced on bulk W by the nanosecond laser apparatus and by more conventional fusion-relevant high heat fluxes irradiation techniques (i.e. ms lasers and electron beams). It was demonstrated that, by considering the heat flux factor (HFF) as the irradiation comparison term between the various irradiation sources, similar thermal effects thresholds are obtained under similar heat flux factors. This required, for the first time in literature, the extension of the definition of HFF to non-constant temporal sources (i.e. Gaussian profiles) in the nanosecond regime. A numerical code was also completely developed and validated for predicting the thermomechanical response of nanostructured coatings during nanosecond laser irradiation.

Exploiting the above techniques, the second task of the thesis was the characterization of the thermomechanical properties of as-deposited nanostructured coatings. These properties were determined and deeply discussed in terms of their relation to the specific nanostructure, morphology and chemical composition of the samples.

The developed method resulted really sensitive to nanostructure changes, and could provide quantitative information about various thermomechanical properties, like the stiffness, the thermal expansion coefficient and residual and thermal stresses. In particular, it was observed that the differences of these properties between various samples were strictly related to mass density (ρ), crystallites size (D) variations and to material composition. This explained why amorphous metallic W coatings, being characterized by a mass density about 60% the bulk W one and negligible crystallites dimension, showed a loss of stiffness by about 40% with respect to the nanocrystalline counterpart. The softening of the coatings, in turns, resulted in an increase of the thermal expansion coefficient. A peculiar nanostructure was found for crystallites size be- tween 4 and 10 nm. This structure was called ultra-nano- crystalline, and its related thermomechanical properties resulted from a non-obvious interplay between the crystalline fraction and the averaged size of the crystalline seeds and void fraction. Moreover, the properties of amorphous W coatings resulted to be strongly affected by the chemical composition of the samples. In particular, the formation of amorphous W-oxide phase drastically lowers the stiffness, as the O/W stoichiometric ratio increases. The addition of N_2, instead, gave the amorphous phase a higher stiffness when W_2N compounds form.

The last task of the thesis was devoted to the investigation of the behavior of these coatings under thermal loads. In particular the coatings were tested under two different fusion-relevant scenarios that mimic both steady and transient thermal loads. For the former case, standard annealing treatments were exploited to investigate the behavior of amorphous W and W-oxide coatings at ITER-relevant steady operating temperatures. The crystallization behavior was thus investigated. In general, all these tests have demonstrated that the exposure to high temperatures, which, however, are far from the recrystallization temperature of bulk W, drastically changes the properties of the coatings. This could represent a crucial aspect also for tokamak environments, where PFCs will be eventually coated by layers with unknown pristine properties, that could also change during machine operation. Finally, the behavior of W nanostructured coatings was investigated under pulsed thermal loads mimicked by nanosecond laser irradiation. To this purpose, the coatings were tested under both single and multishots laser irradiation, and the heat flux factor thresholds for the different thermal effects were obtained for the various structures and morphologies. Damage thresholds were found to be strongly affected by the porosity degree of the coatings, being lower as the coatings become more porous. This was observed for the melting and the cracking threshold, which, in turn, strictly depend on the thermal diffusivity and the yield stress of the material. Reduced thermal diffusivities and yield stresses were thus obtained simply starting from the bulk values and by applying a reduction factor given by the variation of the coating mass density with respect to the bulk one. The obtained values, together with all the measured thermomechanical properties of the coatings, were thus taken as inputs for the numerical code, in order to predict the experimentally observed damage thresholds. The computed numerical thresholds were finally compared to the experimental ones obtained under single shot irradiation, showing a very good agreement. This clearly underlined the possibility to predict the thermomechanical behavior of nanostructured coatings without considering the real complex coating structure and morphology.

INNOVATIVE METHODS FOR ON-LINE CONTROL-ORIENTED MODELING: AN APPLICATION ON THE TRIGA REACTOR

Sara Boarin - Supervisor: Prof. Antonio Cammi

This doctoral work develops an innovative approach to the control-oriented simulation, for application to nuclear reactor plant dynamics of current GEN-III and new GEN-IV. The TRIGA-MARK II in Pavia allowed model validation with experimental database.
The novelty consists in:
advancements in the characterization of the TRIGA physics and modeling;
new methods and approaches to the reactor plant dynamics prediction.

A non-linear model of the plant, with simplified geometry and spatial layout, is built with a twofold approach:
a-causal, declarative, in Dymola OOM simulation environment;
traditional, causal, in Matlab-Simulink environment.
Linear stability analysis is performed on the ODE system implemented in Simulink: stability regions are investigated by calculating the eigenvalues of the matrix of the dynamics, with respect to different values of fuel and moderator temperature reactivity coefficients.
The modeling scope includes the reactor pool, whose thermal inertia is key to the system dynamics, natural circulation across the core, cooling system and core reactivity:
fuel temperature coefficient is modeled with experimental fast power transient at different power values;
moderator temperature coefficient is modeled by elaborating results of previous research, based on Monte Carlo N-Particle transport code and thermal-hydraulic FEM COMSOL Multiphysics®;
Poison concentration dynamics is modeled and anti-reactivity has been calculated with experimental data. The whole model is validated with experimental transients performed by the candidate in March-May 2015, in collaboration with the INFN-Milano Bicocca.
The plant model simulation represents the best 'prior' knowledge of the system physics. This is nonetheless affected by simplifications and uncertainty due to incomplete understanding of the plant physics (e.g. friction factors, coolant flow regime, heat exchange model and parameters). This holds especially for innovative GEN-IV technology. On the other hand, the drawback of a control strategy based on measurement data alone is that measures come from few points in space and many relevant variables are not accessible by sensors (not observable). Measurements may be affected by noise or systematic error.

The control-oriented strategy proposed in this work is an innovative combination of the best available techniques to improve the accuracy of the dynamics prediction. It relies on the Kalman Filter (KF), an iterative prediction-correction algorithm that assimilates measures from the real system to improve 'prior' estimates.
If the relation between observables and state variables is given, the 'hidden' processes are predicted through an inverse problem technique.
KF is suitable for application to GEN-IV where harsh physical and chemical conditions limit the scope of use of sensors or their lifetime.
The Extended KF (EKF) is suitable for application to non-linear system dynamics and consists of a dynamic linearization of the state space system and the application of the standard KF equations at each time step.
Convergence and consistency of the EKF are not granted, as for simple linear filter. Since EKF approximates the posterior probability $p(X_n|Z(0:n))$ as a Gaussian, it may have poor performance in some cases when the true posterior is heavily skewed or multimodal. EKF can be designed to produce good estimates of a non-linear system, provided that it is fine-tuned with suitable design parameters: the steady-state performance of the filter is uniquely determined by process noise covariance Q, observation noise covariance R and initial covariance matrix of the prediction error P(0). Unlike the case of linear filters, there is no general methodology for EKF parameters initialization; in complex system this task may become hard and critical.
This work adopts Particle Swarm Optimization (PSO) as a solution to the issue of EKF initialization. PSO is a stochastic optimization method where the position of a particle corresponds to a candidate solution of the optimization problem (i.e. a set of values for the EFK initialization). Particles move around the space testing new parameter values, to decrease the value of a properly defined object function. Their interactions result in iterative improvement of the quality of problem solutions over time, according to specific rules. PSO is faster than Genetic Algorithms and unlike evolutionary algorithms it does not use selection. The use of the PSO for the automatic tuning and initialization of the EKF is an advancement brought by this research work about the issue of EKF consistency and convergence. Results of EKF predictions show an accurate tracking of the process dynamics without overshooting or diverging. Stability and consistence are allowed by the PSO application to the EKF parameters initialization.
Some 2nd order effects on prediction accuracy may be further investigated or detailed:
the model is lumped parameter in some key elements (e.g. reactor pool);
true value of friction factor in core is unknown. Small variations can sensibly affect the mass flow rate in core and the neutron dynamics.
heat transfer model between fuel and coolant is averaged on the whole core.
reactivity feedback coefficient of fuel temperature is calculated by fitting experimental data, based on a model whose uncertainties are not 'closed' (according to the above mentioned issues).
Research developments may include:
CFD simulation to provide insight on the flow regime and on the heat transfer conditions in the different core channels;
comparison with alternative prediction methods (e.g. Particle Filtering), in terms of prediction accuracy and computational effectiveness.
application of Reduced Order Methods, to further streamline the computational task, improving simulation accuracy and detail.
Bias introduced by systematic error in measurements is an open issue, which is not addressed by the EKF.

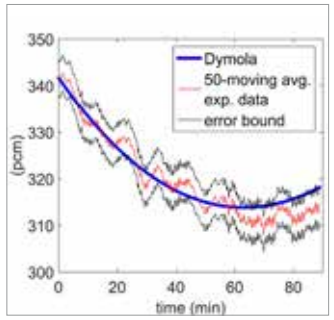

Fig.1 - Experimental transient: values of control rod reactivity. Dymola simulation, moving average of experimental values

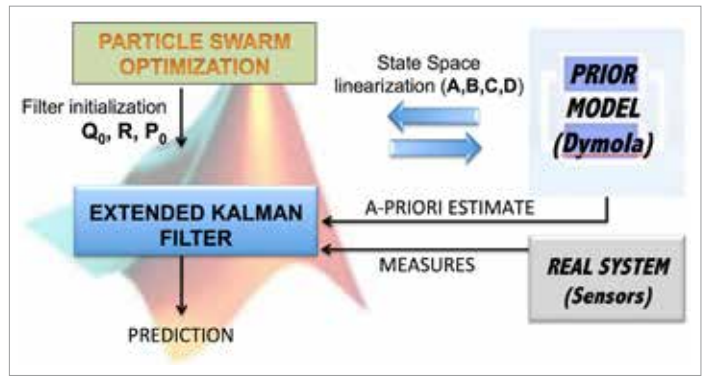

Fig. 2 - Conceptual scheme of the control-oriented simulation tool developed in this PhD research work

BIOGAS UPGRADING BY ABSORPTION AND ADSORPTION TECHNOLOGIES

Federico Capra - Supervisor: Prof. Emanuele Martelli

Biomethane is gaining interest, since it is a renewable surrogate of natural gas from fossil origin, and can be used both as a fuel in the transport sector and for high efficiency power generation, exploiting the existing natural gas infrastructure. In order to accomplish such results, biomethane has to be produced starting from biogas (a mixture of methane and carbon dioxide) performing a separation between its components, denominated biogas upgrading. There is a wide range of technologies available to that extent, but none emerged as clear benchmark for the typical sizes of biogas producing plants (500-1000 Nm^3/h), due to the large variability in both costs and performances reported in the literature and by vendors. The development of newer adsorption materials has raised interest in the application of Pressure & Temperature Swing Adsorption (PTSA) to biogas upgrading, since such process exhibits moderate energy consumption (of both thermal and electric power) and operational easiness (no solvent flow has to be handled).The present work aims at evaluating the potential of PTSA processes applied to biogas upgrading potential, with special focus on novel sorbent (alumina impregnated with amines). To such extent, the performances of PTSA processes are compared to the ones of two other benchmark technologies: water scrubbing and chemical scrubbing. Water scrubbing is actually the most diffused upgrading technology, it uses water to absorb carbon dioxide and it is simple and effective. On the other hand, water scrubbing shows large energy consumption in order to regenerate the solvent. Chemical scrubbing looks promising, since the use of chemical solvents (generally amines) allows higher CO2 capture capacity and consequently a reduced energetic consumption. On the other side, such technology is more expensive and more difficult to operate. A methodology for the comparison of biogas upgrading technologies, considering energetic, environmental and economic aspects is established: a common framework for the analysis is defined, in which the energy demand of the upgrading process is satisfied by burning part of the biogas available in a Combined Heat and Power unit. Then, for the three different upgrading technologies i) accurate first principle model are developed/tuned to solve the mass and energy balances of the plants. ii) an economic model is established, to estimate the cost of every equipment unit ii) a multi-objective optimization is performed to identify the optimal trade-off curve between energetic efficiency and cost of each technology. The optimization of absorption based technologies is carried out with available optimization tool, whereas an ad-hoc optimizer, named MO-MCS is developed for tackling the optimization of TPSA processes. The optimisation of adsorption based processes is a well-known problem, since heuristics and engineering considerations may allow to determine some of the decision variables, while others, such as the duration of time steps, are extremely difficult to predict, given the dynamic nature of such processes. Moreover, constraints on the purity and recovery of the products have typically to be considered, and the solution of the model describing equations is computationally intensive. The proposed MO-MCS algorithm is global and make use of models of the objective functions in order to save computational time. Such algorithm proved to outperforms other available ones, as shown in Figure1, and then is applied in this work to determine the optimal working conditions of two proposed adsorption cycles. Finally, the comparison between the optimal performance trade-off curves is carried out, and conclusions are drawn. The advantage of this approach is that the optimal operating range of each technology is explored, and the results are not biased by the uncertainty of cost related data. On the other side, the final choice of a technology from a user entails the selection of a single configuration among the ones laying on the optimal trade-off curves. Once the trade-off curves between efficiency and cost are known, they represent a valuable tool for the final user who can select the best configuration based on application specific conditions (operating costs, valorisation price of biomethane and electric power). The TPSA process with the novel material, shows the lower specific equipment cost when adopting a six-step adsorption cycle, followed by water scrubbing technology and by chemical scrubbing. From the efficiency point of view while, the TPSA processes with a simpler four-step cycle outperforms chemical scrubbing, amine, the six-step configuration and water scrubbing.Also a benchmark adsorbent material (Zeolite X13) is considered, showing unsatisfactory performances. The methane slip is taken as an indicator of environmental performances, since venting methane raises environmental concerns due to its considerable Global Warming Potential. The methane slip allowed by chemical scrubbing process is the lowest, trailed by six-step TPSA, while water and the four step-TPSA show similar methane slips.

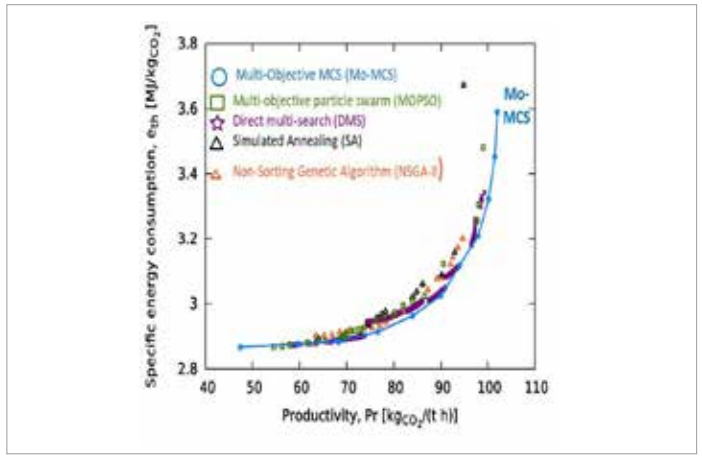

Fig.1 - MO-MCS benchmarking against state of the art optimizers

FUEL-COOLANT CHEMICAL INTERACTION FOR LEAD-COOLED FAST REACTORS BY A COMPUTATIONAL APPROACH

Marta Cerini - Supervisor: Dr. Elena Macerata

In the last century the population growth has determined an increment of energy demand, revealing the no more negligible problem of the impact of energy generation on the environment. Generation IV nuclear systems, fulfilling high standards in terms of sustainability, economics, safety and reliability, proliferation resistance and physical protection, are now under development, because they could contribute to produce clean energy at reasonable costs. Among the new reactor concepts, Lead-cooled Fast Reactors seem to be promising, even if there are technical challenges that still have to be adequately solved. In particular, the knowledge of the chemical compatibility between the nuclear fuel and liquid lead as coolant is a topic of paramount importance for their development and in particular for assessing their safety. In fact, a cladding failure event could lead fuel in contact with coolant both in nominal and accidental operation conditions and the consequences of such event have to be foreseen in order to plan suitable safety systems. The present research work deals with the study of fuel-coolant chemical interaction by means of a computational approach. The system originated from the fuel-coolant chemical interaction is a multi-component and multi-phase complex system, whose chemical composition at thermodynamic equilibrium could be studied by minimization of the Gibbs free energy, starting from the database of thermodynamic data of all chemical species involved in the reaction. Due to the lack of experimental thermodynamic data for the majority of compounds of interest and to the difficulties in performing experimental campaigns, an approach based on the Density Functional Theory combined with the Generalized Gradient Approximation (DFT-GGA) was defined. The DFT method was selected because it represents, among the methods of theoretical chemistry, a good compromise between accuracy of the result and computational costs. The validation process clearly showed that the selected method is able to estimate the formation enthalpy, entropy and heat capacity with satisfactory accuracy for intermetallic compounds and oxides, in both gas and condensed phases. Therefore, using well-known computer programs (Gaussian09 and VASP - Vienna Ab–initio Simulation Package codes), the proposed computational method was applied in a semi-systematic way to estimate the missing thermodynamic properties of several species of interest for the case study, on the basis of the binary phase diagrams and other research works available in literature so that the thermochemical database was implemented.
Furthermore, considering few binary systems as case study, it was verified that the SOLGASMIX-PV like code used for the thermodynamic analysis, correctly foresee the chemical composition of the systems on the basis of the estimated thermodynamic data even if affected by a maximum standard deviation of the same order of that found in the validation process.
Moreover, an attempt was made in order to exploit the proposed DFT-GGA approach to gain information about solubility in liquid Pb of the most important fission products and cladding constituents. In particular, the solubility was investigated by applying the infinite dilution model as implemented in the VASP code. The validation process by comparison with a limited number of experimental data highlighted that the model reproduces qualitatively but not quantitatively the experimental solubility.
The computed solubility values were strongly underestimated, however the trends in function of temperature were reproduced as well as the solubility level among the different elements considered.
In conclusion, at the best of the author knowledge, this research activity studies for the first time the chemical interaction between nuclear fuel and liquid lead under reactor operational conditions. Specially, a computational tool able to systematically estimate missing thermodynamic data was proposed, and a thermodynamic database was implemented enabling the evaluation of the chemical composition of simplified fuel-coolant systems at thermodynamic equilibrium.
In general, the research work performed allows to demonstrate that a theoretical approach can be useful to face a problematic such as the chemical compatibility between fuel and coolant in Generation IV nuclear systems, by getting indications that can actively support and better address the experimental activities, which still remain essential to understand all the phenomena that could occur within these new nuclear reactors.

EXPERIMENTAL AND THEORETICAL STUDIES ON TARGET NORMAL SHEATH ACCELERATION WITH SOLID AND ADVANCED NANOSTRUCTURED TARGETS

Lorenzo Cialfi - Supervisor: Matteo Passoni

Ultra-intense sub-picosecond laser-plasma interaction is a fertile research topic. Laser induced ion acceleration stands out among potential applications for the perspective of providing a compact, cheap (compared to current accelerators) and tuneable ion beam source which can be exploited in: hadron-therapy, neutron/radionuclides production, proton fast ignition and proton imaging. The most experimentally observed mechanism is called Target Normal Sheath Acceleration (TNSA) and can be briefly explained as follows: i) an ultra-intense laser pulse (I> 1018 W/$cm2$) is focused to a target (typically micrometric foils). ii) due to the interaction with the laser pulse it reaches plasma state and an electronic population is heated to high energies (MeVs). iii) these electrons expand through the target and eventually into the vacuum, creating a charge separation responsible for the electrostatic field which accelerates ions on the rear surface up to tens of MeV. Coherently to this description, electron heating plays a crucial role in the acceleration, thus a better control over this process could lead to the development of optimized techniques and, as a consequence, to better performances (e.g. higher maximum energies). The first experimental observations of TNSA were obtained with micrometric solid targets (SLT), in recent years advanced target configurations were proposed. At this purpose, nano-engineered targets have been proven to be ideal candidates. Recent works have shown that using multi-layer targets (MLT), produced by the deposition of a foam layer (~ 10 μm) over the solid one, can increase the laser absorption and ion acceleration capabilities. In the first part of our work we analysed experimental results from two recent campaigns performed in 2014 and 2015 at the PW-class laser facility APRI (GIST, Gwangju, Republic of Korea). As presented in fig. [1], our experimental results demonstrated that under suitable conditions MLTs could outperform SLTs in terms of both maximum energy and total accelerated charge. Fig. [1] also demonstrated that laser polarization strongly influences laser interaction with solid targets while it does not affect MLTs. Besides experimental results, theoretical models proved to be invaluable tools to understand the physics of ion acceleration, providing reliable scaling laws in order to predict experiments and set foundations for future researches. A key parameter in most of the theoretical TNSA models is the electron temperature. At the state of the art one of the most widely adopted scaling with SLTs is the so called ponderomotive scaling. It provides an estimation of the temperature as a simple function of the laser intensity, although it doesn't take in account many parameters that are known to influence laser-plasma interaction deeply, such as laser polarization and incidence angle. Moreover, it is not suitable for advanced target designs. In this work we propose a simple law to predict the electron temperature in a wider range of parameters. This model is supported by an extensive 2D and 3D numerical campaign at different incidence angles, intensities and polarization. We then adopted the new scaling law to extend the predicting capability of a known TNSA theoretical model. In fig. [2] we show the comparison between our theoretical predictions and experimental results at different laser intensities in C polarization. A much better agreement with the old ponderomotive scaling is evident.

As anticipated, MLTs could strongly enhance laser-plasma coupling and, as a consequence, laser induce ion acceleration. Electron heating in this scenario is not trivial, since it involves several processes still not completely understood. We have performed an explorative attempt to use a simple scaling law even in this condition. We supported our model with a 2D numerical campaign, adopting two different configurations: a homogeneous near-critical plasma (8 μm) on a bulk thin (0.5 μm) solid target and a more realistic foam with a micrometric mean critical density formed by nanometric sized over-dense nano particles. This investigation proved a strongly enhanced electron heating with respect to simple plain solid targets, also dependent on the foam nanostructure. We finally introduced two simple scaling laws for the uniform and homogeneous foam, respectively. In fig. [3] we present the comparison obtained matching theoretical predictions with our new estimations of the electron temperature and experimental results. We observed a good agreement and better results were achieved with the nanostructured scaling with respect to the homogenous foam one. In conclusion, in this work we investigated with a combined approach TNSA with traditional STLs and MLTs. Our experiments proved that MLT could be a viable solution to achieve better performances. In this PhD we also studied laser induced electron heating, particularly relevant in ion acceleration scenarios. Our results could be combined with TNSA theoretical models to better predict experimental results.

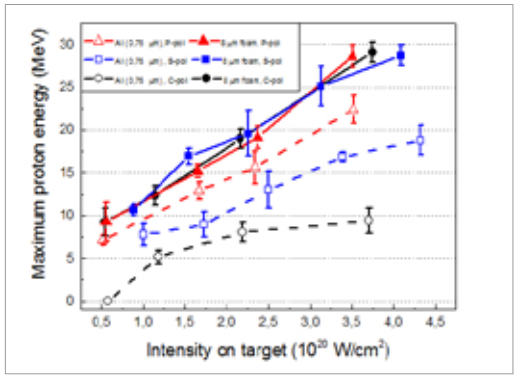

Fig. 1

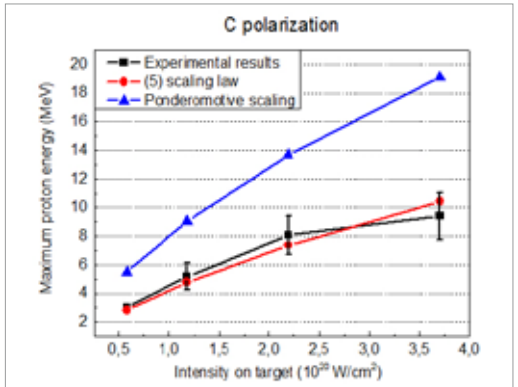

Fig. 2

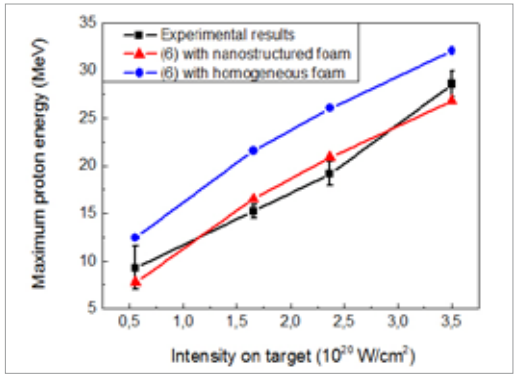

Fig. 3

FLASHING FLOW MODEL FOR INDUSTRIAL ENERGY APPLICATION

Quang Dang Le - Supervisor: Prof. Fabio Inzoli

In this thesis, a reliable Computational Fluid Dynamics CFD modeling approach is developed for flashing flow. To account for phase change process inside throttling devices, an evaporation model, modified from Lee model, is performed that considers thermal non-equilibrium effect (boiling delay) by artificial coefficients. Two-phase stage of flow in evaporation process is described by mixture model with slip effect between two phases. Results of CFD approach are then validated by experimental benchmarks of flow without phase change (air-water flow) and with phase change phenomenon (flashing flow). Besides, sensitivity analysis of artificial coefficients, turbulence models and turbulence quantities is also performed to complete evaluation of model. Validation shows an agreement between CFD model and experimental data for both global and local results.
On the other hand, sizing equation in case of two-phase flow inside control valve is established by adding downstream information into original formula of Leung developed for safety valve. This modification is acceptable due to outlet information is always available for sizing control valves. To validate developed sizing equation, reliable CFD results for a convergent-divergent nozzle from previous stage are used as input data for sizing equation. Convergent-divergent nozzles are used instead of a real control valve in this work due to (i) between nozzles and control valves have singularity in geometry (ii) purpose of thesis is to develop a general two-phase sizing equation for all types of control valve so the usage of nozzle geometry is necessary. Finally, results of validation show a better accuracy of present sizing equation than the others in previous works. Besides, validation also confirms accuracy of semi-empirical sizing equations which is used in industry to size two-phase control valve.
Flash boiling; CFD; Nozzle; Multi-phase flow; Non-Equilibrium Effects; Validation

PROPOSED COMPUTATIONAL FLUID DYNAMICS (CFD) MODEL AND VALIDATION

This chapter is devoted to a presentation of a proposed CFD model for flashing flow and validation

Multi-phase flow model

In this thesis, the mixture model has been applied to model two-phase flow. Within the mixture approach, a slip model is used to couple the two phases (liquid and vapour).

Phase change model

In this work, the Lee model is modified to become the phase change model driven by pressure. In addition, the thermal non-equilibrium effect is inserted into the present phase change model by "artificial coefficients" as defined in the following of section.
The first step is to define the vapor transport equation, which is solved along with the other governing equations:

$$\frac{\partial(\alpha_v \rho_v)}{\partial t} + \nabla \cdot (\alpha_v \rho_v \vec{v}_m) = \dot{m} \quad 1.1$$

The change of phase source terms is derived from (Hertz, 1882) with the evaporation-condensation flux at the interface

$$F = \beta \sqrt{\frac{M}{2\pi R T_{sat}}} (P_{sat} - P^*) \quad 1.2$$

where is molar mass. is the partial pressure at interface on the vapor side with value close to saturation pressure, . Eq. 1.2 can be inserted into the vapor transport equation as a source term, should be modified to take into account the interfacial area density. Particularly in this thesis, the interfacial area density is applied following the proposal of Liao and Lucas (Liao & Lucas, 2015), as defined in Eq. 1.3:

$$A_i = (6\alpha_v)^{2/3} (\pi N_b)^{1/3} \quad 1.3$$

Combining Eq. (1.2) and Eq. (1.3), the source term for the vapor transport equation at the interface is defined as:

$$\dot{m} = F A_i = A_i \beta \sqrt{\frac{M}{2\pi R T_{sat}}} (P_{sat} - P^*) \quad 1.4$$

In this paper, the formula of the vaporization pressure, as defined in Hinze (Hinze, 1975), is used to account for local turbulence effects. It reads as follows:

$$P_v = P_{sat} + 0.195\rho k \quad 1.5$$

Finally, considering Eq. 1.5 along with Eq. 1.4, the source term for the mass flux at the interface is as follows:

$$\dot{m} = F A_i = A_i \beta \sqrt{\frac{M}{2\pi R T_{sat}}} (P_v - P^*) \quad 1.6$$

CFD validation

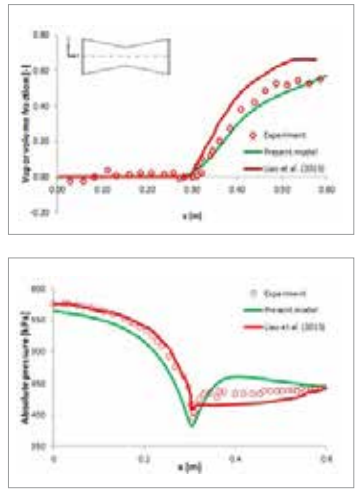

Figure 1.1: Averaged vapor fraction and absolute pressure along nozzle compared to experimental data in (Abuaf, Jones, & Wu, 1983) and (Liao & Lucas, 2015)

PROPOSED SIZING EQUATION AND VALIDATION

In case of liquid mixed with its own vapor flowing through a throttling device, additional complexity arises compared to frozen flow due to heat and mass transfer between the phases. For this reason, there is no formula in standards (IEC, ISO, etc.) for sizing control valves for liquid/vapor mixtures flow. However, some models without confirmation of accuracy are published including SUM, EQUIVALENCE model in (Driskell, 1974), OMEGA model in (Leung, 1996) and HNE-DS in (Diener & Schmidt, 2005).In this project, a proposed sizing equation is proposed by only modifying omega parameter, , in (Diener & Schmidt, 2005) which is the most important factor for phase change phenomenon with non-equilibrium effect inside devices. New omega parameter, , requires information of the outlet mass averaged specific volume. Practically, this approach is more suitable for control valves when information of the outlet is always available.

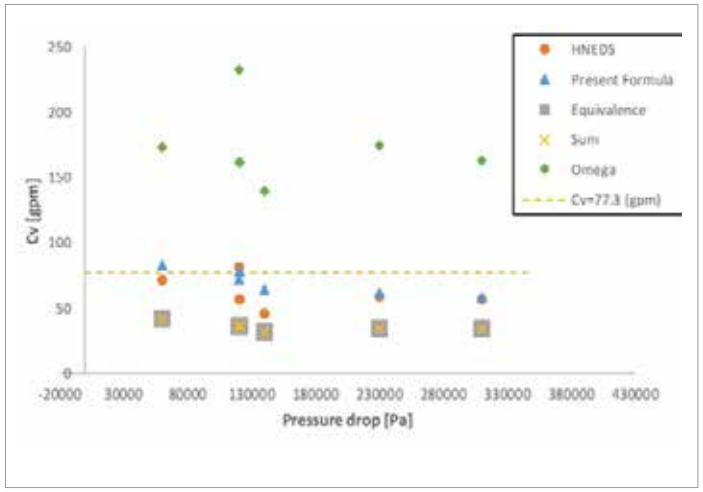

Figure 2.1: Sizing equations in case of (Abuaf et al., 1983) Cv=77.3

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DEVELOPMENT OF A MICRO-COGENERATION SYSTEM BASED ON MEMBRANE REACTOR AND PEM FUEL CELL

Stefano Foresti - Supervisor: Giampaolo Manzolini

In the last decades the sensibility toward the environmental aspects and the climate changes increased worldwide. The scope is to reduce the greenhouse gases and pollutants emissions by increasing the energy efficiency and the share of renewable energy sources. Greenhouse gas emissions mainly consists of CO2, from coal and hydrocarbons combustion in industrial processes, transportation, heat and power production. Micro-cogeneration, i.e. in loco simultaneous production of heat and power, is an effective way to increase the efficiency in the domestic sector, which represents a large share of the overall energy consumption (about 30% in EU countries). A possibility is the substitution of hydrocarbons with the so-called "second generation" bio-fuels, like bio-ethanol, also in the micro-cogeneration devices. This work deals with the development of an innovative micro-cogeneration system fueled with bio-ethanol for off-grid applications, within the EU-funded FluidCELL project. Bio-ethanol is selected as feedstock because renewable, easy to store and not toxic fuel. The system is based on membrane reactor technology for hydrogen production and PEM fuel cells for high-efficiency electricity generation. The most relevant innovations relies in the fuel processor, a fluidized bed autothermal reformer with suspended Palladium-based membranes, that produces high-purity hydrogen in one vessel only, differently from conventional fuel processors, which adopt several steps (reforming and high- and low-temperature water-gas shift). Small-scale cogeneration systems with conventional fuel processor and PEM fuel cells are at early stages of commercialization. They are simulated and their performance are assumed as benchmark to compare the improvement that can be obtained with the innovative concept. The electric efficiency of conventional systems, for all the configurations investigated, results below 35% (based on ethanol lower heating value).

As first step a preliminary analysis of the innovative system is carried out to investigate the conditions that lead to electric efficiency higher than 40%, which is the target of the FluidCELL project. The system is rated at 5 kW_{el}. The core of the system is the membrane reactor, where the ethanol-water-air mixture undergoes auto-thermal reforming reactions producing hydrogen; hydrogen is removed by the Palladium-based membranes and obtained, in theory, as a pure stream. In particular two membrane reactor configurations are analyzed to enhance the permeation: the case with sweep gas and the case with vacuum pump. Based on the sensitivity analysis the design conditions for the prototype are defined. The main concern is the reliability of the membranes assembly inside the reactor that could degrade and separate hydrogen with lower purity than expected. Hydrogen quality affects the fuel cell voltage and consequently the overall system performance; therefore a guard system to limit CO entering the fuel cell and fuel cell control strategies are also investigated. Experimental tests performed on different palladium-based membranes (with metallic and ceramic support) and membrane reactors show the potentiality of hydrogen production with this technology. Experimental results are then used to calibrate the parameters of a detailed model of fluidized bed membrane reactor. The hydrogen output computed with the detailed model, depending on the operative conditions, is around 10% lower than the one computed with ideal models when vacuum is used on the permeate side; and up to 50% lower when sweep gas is used: in this case gas diffusion across the porous support is identified as the limiting phenomenon.

The operation of the PEM fuel cell stack (with Pt-Ru catalyst at anode side) is experimentally examined reproducing the conditions that may occur in the real system when it is integrated with the reformer: the fuel composition can shift from pure hydrogen to hydrogen-rich mixture depending on the membranes selectivity and the anode off-gas recirculation. Results show that the voltage loss caused by hydrogen dilution by inert gases, up to 30%, is small compared with that caused by few ppm of CO (up to 40 ppm) when the cell is operated in flow-through mode. In dead-end mode very small amount of inerts in the feed (0.05%) accumulates in anode channels and causes fast voltage drop, recoverable by frequent purges. Measurements of the local current on the cell surface allow describing also the dynamics of the CO poisoning for the specific geometry of the bipolar plates of these cells. CO poisoning starts from the anode inlet and moves to the anode outlet, the most penalized region in steady state conditions. A detailed model of fuel cell is developed and validated against the experimental data. Finally the complete system, integrating the detailed models of membrane reactor, PEM fuel cell and balance of plant, is simulated in order to analyze different aspects: (i) partial load operation: the curves of electric and thermal efficiency cover the range 1-5 kWel, being the minimum set by the catalyst bed fluidization inside the membrane reactor; (ii) annual performance, to satisfy the heat and power demand of a semi-detached house without connection to the electric grid, in two different climatic regions (Italy and Germany). Different scenarios are assessed for comparison: the m-CHPs considered are an internal combustion engine, a PEMFC unit with conventional fuel processor and the innovative FluidCELL unit, coupled with either a boiler or a heat pump for the residual heat supply; (iii) effects of low-selectivity of the membranes on the PEM fuel cell and the management of the anode off-gas recirculation.

Main conclusions drawn from this work are the following:

(i) fluidized bed membrane reactor outperforms conventional fuel processors in term of fuel conversion. The main limit for the sweep gas layout in case of membranes deposited onto thick supports comes from slow gas inter-diffusion across the support;

(ii) global performance of the m-CHP unit are evaluated for different off-grid scenarios (cover both electric and thermal load of a detached house): annual simulations of the operation show that the innovative system outperforms the m-CHP units based on conventional fuel processor or internal combustion engine, especially as the thermal load is reduced in favor of the electric load, i.e. coupling the m-CHP unit with a vapor-compression heat pump instead of a boiler. However, the advantage of PEM-based system over internal combustion engine reduces over the time due to cells degradation: for example the fuel saving with respect to the ICE, is expected to reduce from 34% to 18% after five years of operation.

(iii) in case of low-purity hydrogen feeding to the PEM fuel cell with anode off-gas recirculation, the optimal hydrogen vent fraction is around 0.1%-0.3% of the stoichiometric amount;

Tests on the prototype will be performed to measure the effective performances of the complete system, as well as to evaluate the level of maturity of this technology and take advantage by this experience for a better design.

Keywords: micro combined heat and power; fluidized bed membrane reactor; polymer electrolyte membrane fuel cell; bio-ethanol.

MODELING, OPTIMIZATION AND EXPERIMENTAL EVALUATION OF SOLAR DIRECT STEAM GENERATION FOR INTEGRATION INTO INDUSTRIAL HEATING PROCESSES

Antoine Frein - Supervisor: Prof. Mario Motta

1. Objectives of thesis work

a. Research theme

The project scope is to investigate the application of medium temperature [100°C - 250°C] Direct Steam Generation (DSG) from a Linear Fresnel solar reflectors (LFR) into industrial heating processes.

b. Type of study

The type of study is both numeric and experimental. Detailed numerical models are developed and validated on the Direct Steam Generation Laboratory. Then, they are applied to a real case study, 222 kW_{th} linear Fresnel solar field in Jordan, to characterize the main constraints of this kind of plant. Finally, innovative control strategies and innovative designs are proposed and tested to improve the overall performance and plant stability.

c. Originality

The industrial sector has been identified as a high-potential and still largely unexplored application for solar thermal. In fact, medium temperatures solar DSG is far from being a mature technology for industrial applications and their market penetration has been slow and difficult. Published performance results from existing installation, both in industrial sector and power generation, are yet scarce. The opportunity to present results from Laboratory test and real case study (RAM, Jordan) is unique and it leads to improve the state of the art of this application. A new methodology for solar field design and flow pattern monitoring is developed and an optimized control strategy and plant layout are proposed

2. Research framework

a. Numerical models

Three numerical models have been developed with three different objectives. A first model is developed to study performance and behavior (pressure drops, steam drum level, flow pattern) of existing solar plants. It is applied to the test laboratory and to the specific case study. It highlights specific transient phenomena that have to be studied more in details under different assumptions. The first phenomena is the effect of the moving evaporation start point within the absorber, done with the dynamic Model 2. The second phenomena is night heat loss of the solar system characterized with the dynamic Model 3.

b. Experimental activity

A DSG bench was developed under restrictive budget limitation at the Energy department of Politecnico di Milano (POLIMI), with the objective to validate Model 1 and some of its assumptions:
pressure distribution over the recirculation loop;
head loss correlations
implemented in the numerical model;
validation of flow pattern map outside of its boundary conditions.
The latter is the most original point as the flow pattern maps used in Model 1 is an extrapolation of Kattan Thome Favrat (KTF) correlations, which have been developed and tuned for refrigerant in small diameter pipe at low pressure. The map is compatible for refrigerants and it is not demonstrated that they are suitable for steam-water systems as its surface tension and density ratio are high with respect to the refrigerant database. In the present study, the KTF correlations have been used outside their boundary conditions for water flow in larger diameter pipes (70 mm compared to 8-20 mm) and higher pressure (3-25 bar compared to 1.1-8.9 bar). The flow pattern transition curves encounter with solar DSG for industrial heating processes delimited the following flow patterns: intermittent, stratified wavy and annular. The experimental activity validates the use of water instead of refrigerant for these specific transition curves. Figure 1 shows the good agreement between KTF correlations and the experimental tests.

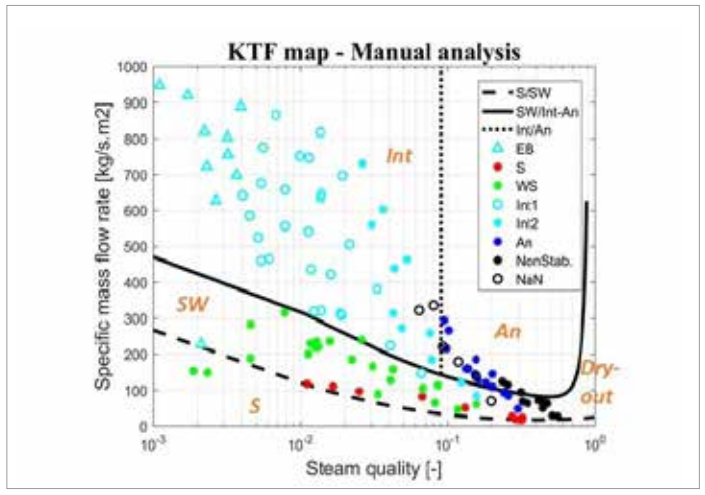

Fig. 1 - Flow pattern maps validation for water as medium

c. Analysis and case study (RAM)

A system operation with biphasic flow requires a specific optimization to limit the pressure losses, maximize the heat transfer rates and avoid the harmful flow patterns. Requirement as pump cavitation protection, natural circulation, pressure stability should be satisfied for each plant condition. This analysis is applied to a real case study (RAM plant installed by Industrial Solar) for two distinct periods one in winter (two weeks) and one in summer (two weeks). It is based on the comparison between a validate numerical model 1 and monitored data. The first step consists on a daily analysis of the mass and energy balance for the two specific periods, called global analysis. Then a detailed analysis is applied to one sunny day in winter and one in summer. It consists in the analysis of recirculation pump head loss, liquid level variation of steam drum and daily flow pattern analysis.

d. System optimization

The system optimization consists in applying the validated numerical models to improve the solar DSG design and control strategy for the specific application of industrial process heat. Different levels of optimization are investigated. The first one is focusing on the methodology to design the solar field layout (parallel vs series, optimal mass flow rate) for a MW plant based on Model 1. The second and third optimizations are focusing on unexpected behavior highlights in the case study. The second one analyzes the effect of fast moving evaporation start point impact with the numerical Model 2 and third one analyzes how night heat loss could be reduced with an improved control strategy. The improvement quantification is done with Model 3. The last point summarized the various good practice design already presented in the previous chapters.

Fig.2 - Linear Fresnel Reflectors at RAM plant in Jordan (source: Industrial Solar)

Abbreviations:

DSG:	Direct Steam Generation
LFR:	Linear Fresnel Reflectors
CSP:	Concentrated Solar Power
EB:	Elongated Bubble
S:	Stratified
SW:	Stratified Wavy
Int:	Intermittent
An:	Annular

DEVELOPMENT AND MODELLING OF A WATER-AMMONIA HEAT TRANSFORMER TO UPGRADE LOW-TEMPERATURE WASTE HEAT

Silvia Garone - Supervisor: Prof. Mario Motta

In a growing energy demand scenario, exploiting industrial waste heat has relevant potential to improve the overall efficiency and reduce energy needs, emissions and costs. However, the main hurdle to waste heat use is often represented by its low temperature, making its integration in other processes challenging if not impossible without increasing the waste heat temperature.
Absorption heat transformers are one of the possible technologies to enhance waste heat recovery. They are thermal-driven devices to upgrade heat without the need of higher temperature sources or significant electricity consumptions. Indeed, their useful effect (raising the temperature level of a heat source) is brought about by degrading roughly half of the heat input itself and rejecting it to a cold heat sink.
In this way, the other half of the heat input is made available at higher temperature, making its exploitation easier. A particularly interesting application of this technology is to ease the integration of otherwise useless waste heat in district heating networks, as such an application could benefit from an optimal phasing between load and performances. In fact, both COP and heat duty of a heat transformer increase when a lower condensation temperature is available, as in colder days of peak heating demand.
This work focuses on such an application to improve very low-grade waste heat exploitation. Therefore, a heat transformer, able to recover heat at T<65°C and providing temperature lifts of ≈20K, has been developed and tested.
To work in such a low temperature field, up to now not investigated by experimental studies, water-ammonia was chosen as a working fluid. The choice of a pair well-known in the absorption field, but never used in heat transformers, is the novelty of the work, which has to deal with the issues related to the fact both species are volatile. For this reason, the research was carried out both experimentally and through thermodynamic simulation.
Major outcomes of this research are the achievement of a stably working prototype with good performances and the interpretation of the experimental results through a tuned model, able to give a full picture of all cycle parameters.
Assisted by thermodynamic simulation, testing was carried out on a small-scale prototype to define the most relevant hardware choices. In particular, designing an effective liquid-vapour separator was needed to manage the solution at restrictor outlet, normally with a high vapour quality. The geometry of the throttling valve and the solution charge were optimized, and a stably working prototype was obtained.
The final machine performances were characterized in an extensive experimental campaign, where both external and internal parameters were measured. Though heat duties and working range have a margin of improvement if pressure drops in the solution heat exchangers are limited, the performances (COP and Gross Temperature Lift) of the machine were quite in line with the expected values. Indeed, the experimental results seemed at least comparable with those of similar experimental studies, though carried out in different temperature ranges.
Nevertheless, the previously developed thermodynamic model, based upon assumptions commonly reported in literature, is not reliable in reproducing exactly the machine performances and trends. A new tuned model was developed, putting some of the assumptions into question and replacing them with empirical relations built upon the experimental data.
The resulting grey-box model, once validated, could provide more insight on non-measured variables such as concentrations and vapour quality. The main conclusion is that, despite the improvements in the liquid-vapour separator, which indeed allowed the cycle to work stably, a small amount of liquid solution is still dragged in the refrigerant circuit by the fast, two-phase flow at restrictor outlet, and this affects steady state performances as well as stability in off-design conditions.
As an alternative solution to improved separators, which would likely be extremely bulky and therefore scarcely suitable for industrial applications, the tuned model was used to study possible cycle improvements. In particular, an additional internal heat recovery could easily halve the vapour quality at restrictor outlet, making the flow easier to manage. The COP of the cycle is not expected to vary (apart from the improvements due to the expected refrigerant concentration increase), and some heat load would shift from the evaporator to the generator, a more complex exchanger (a falling film was used in the prototype). However, the study also showed that the theoretical advantage of using a falling film exchanger is not exploited in the real machine due to the separation issues. Replacing the falling film generator with a plate heat exchanger becomes a promising future development, which is expected to improve performances (especially if coupled with the aforementioned additional heat exchanger) thanks to the fact it normally contains a two-phase flow, while at the same time reducing weight and cost of the machine.
Finally, a possible alternative working fluid was examined, since many studies in literature claim that NH_3-$LiNO_3$ can ensure better performances than NH_3-H_2O, without the limitations of water-salts mixtures. However, thermodynamic simulations showed that, though ammonia lithium nitrate could theoretically achieve a better COP, heat transfer coefficients would be more or less halved as a consequence of the different thermos-physical properties (namely, higher viscosity), leading to the need of sensibly higher exchange areas. This is probably not a suitable solution for heat transformers, where investment cost is already a hindering factor and COP has a limited significance, since waste heat is used.

EXPERIMENTAL CHARACTERIZATION OF STEAM TURBINE STAGES: EFFICIENCY, BLADE-ROW INTERACTION, FORCES AND OFF-DESIGN CONDITIONS

Giacomo Gatti - Supervisor: Vincenzo Dossena

Steam turbines are a fairly old piece of energy conversion technology. However, they are still the core of most power production plants, accounting for about 80% of the total worldwide energy production. It is important to put this into context by analyzing the current scenario in terms of sources, which are strictly related to the conversion technology. According to the EIA's International Energy Outlook 2016 report, renewables are expected to show the highest growth rate, pushed by growing concerns on the environmental impact of technologies based on fossil fuels. However, the combined share of Petroleum, Nuclear and Coal based production is still expected to account for more than 40% of the market in 2040, and these all require steam turbines for the conversion. At the same time, the low price of Natural Gas drives the growth of this source, which is increasingly exploited in combined (gas-steam) cycles for efficiency improvement. Indeed, even small increases in conversion efficiency yield substantial reduction of greenhouse gas emission. Considering this picture, it should come as no surprise that research on steam turbines is still a relevant topic.

The framework of this work is a research contract with General Electric for the performance measurement and aerodynamic characterization of four different steam turbine stage designs. They have been thought specifically for Oil&Gas application, where steam generated by other chemical processes is available. In this case, the turbine usually drives a compressor instead of an electrical generator.

Typically, a designer has a few constraints, such as the full machine size (i.e. a limit on the maximum number of stages), the required power output and the mass flow rate; these drive the choice of the stage design. In fact, each stage is designed to cover a certain range of specific work coefficient at assigned flow coefficient. Together, they form a "library" from which the designer can chose according to the aforementioned constraints. In particular, the stages object of this work are all intermediate-pressure (IP) stages, shrouded, with degree of reaction around 0.5 and a blade aspect ratio of about 3. They differ in blade design and solidity or, in other words, in the work-mass flow space they can cover.

Blades are nowadays designed mainly by using numerical methods, which combine three-dimensional unsteady CFD and optimization algorithms (state of the art in industrial practice). More specifically, RANS simulations are still the most widely used approach in industry. The advantage is a relatively modest computational power required, traded for the necessity to introduce models for the Reynolds stress tensor. Over the years many turbulence models were proposed, each of them typically tailored for different flow conditions. For turbines internal flow, variations of the two-equations k-omega model are the customary choice. While the main flowfield features are usually well reproduced, the efficiency value prediction is more critical. This is particularly true if, for instance, a boundary layer transition or a significant separation region are present. Also, certain geometrical details of a complex three-dimensional multi-stage domain (e.g. seals, cavities, etc.) might be neglected and substituted by simplified models, in order to minimize the computational time. For all these reasons, an experimental validation is still required both for performance and local flowfield predictions, and this is where the present work takes place.

This thesis focuses on four major themes, all related to the experimental characterization of these stages.

The first topic is the Performance Measurement. More specifically, two possible definition of the stage efficiency are presented: the "thermodynamic" efficiency and the "torque efficiency". These two definitions require different measurement setups and are characterized by different accuracy and repeatability. All the tests presented in this work use air as working fluid; while this allows for a great reduction of rig complexity, it also poses some challenges related to the impossibility to operate in strict Reynolds similarity, and to the much lower power generated by the turbine. Moreover, the low available enthalpy drop means that even small errors heavily impact the results of efficiency measurements; thus, great care has been dedicated to define methodologies to correct the experimental errors as much as possible.

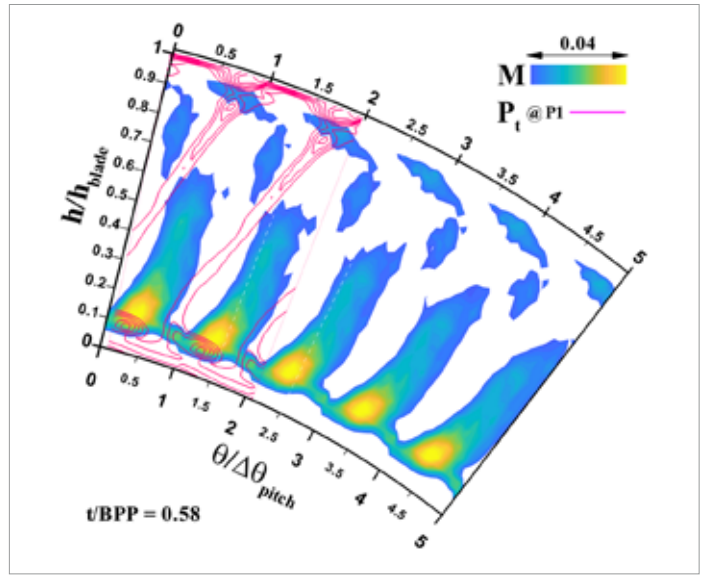

Fig. 1 - Snapshot of Mach flowfield downstream of the rotor. The contour levels cut-off threshold has been set so as to highlight the loss regions. In red are reported the contour lines of Pt downstream of the first stator.

The second topic is the Aerodynamic Characterization of the stages. The aim here is to present an accurate and detailed analysis of the local flowfield. Interstage traversing was performed with pressure probes, with both steady and unsteady techniques. One of the objective is to provide an extensive dataset to be used to calibrate the numerical tools. Moreover, the blade-row interaction phenomena are identified (e.g. [Fig. 1]), and the impact of secondary structures on losses is assessed. A methodology to extend the time-resolved acquired data over the full annulus has also been implemented. Visualizing the flowfield in this way opened the possibility to study the propagating patterns generated by the different rotor/stator blade counts.

The third topic is the Estimation of the Aerodynamic Forces on the rotor using pressure probe measurements. The design of a stage cannot neglect the mechanical loading on the rotor generated by the aerodynamic forces. For example, when a FEM analysis is performed, it is necessary to know the forces exerted by the flow in order to calculate the internal stresses. The problem is, the usual ways to measure these forces is by means of piezoelectric pressure sensors installed on the rotor blades. While rigorous, this method requires a telemetry system, at a non-negligible cost. In this work, a simpler but approximated methodology based on time resolved pressure measurement is proposed, and its accuracy assessed.

Finally, the fourth topic regards the Off-Design Conditions. More specifically, one of the design constraints is the full machine size, as mentioned above. This last chapter analyses the behaviour of a stage when installed as first reaction stage without a control stage in front. This can translate in severe incidence conditions on the first stator, which give rise to large separation regions. The aim in this case is to investigate how these loss cores interact with the indigenous secondary structures and how far they propagate throughout the stages. This is important to assess how many stages are penalized in terms of efficiency by these particular conditions.

HIGH PERFORMANCE CERAMIC COATING FOR DEMO BREEDING BLANKET

Daniele Iadicicco - Supervisor: Prof. Marco Beghi

The access to reliable and affordable energy is thought of as crucial to worldwide economic prosperity and stability. Today, nuclear power is totally provided by fission reactors providing about 11% of the global demand of electricity.
According to the **2015 United Nation Climate Change Conference - COP 21 or CMP 21**, held from 30th November 2015 to 12th December 2015 in Paris, nuclear power will play a central role in green house reducing and future energy sustainability.
Nuclear fusion systems offer the possibility of an inexhaustible energy source. It has many potential advantages as compared to nuclear fission system, such as:
 Higher efficiency: the basic fusion reactions are more energetic than the fission reactions and light nuclei are plentiful and easy to obtain.
 Safe and controllable: in case of accident (e.g. LOCA) reaction can be stopped without fuel melting risks.
 More environmental acceptable: fusion products are usually light, stable nuclei rather than heavy radioactive ones.
Today, the **tokamak** configuration (as ITER under construction in France), where a **deuterium-tritium** fusion reaction will occur, is considered the most promising design for the future commercial fusion power plants (e.g. **DEMO**). Energy will be extracted from the 14.1 MeV kinetic energy of neutrons producing in the fusion reaction. This energy will be adsorbed, efficiently channelled inside the **breeding blanket** (**BB**). **BB** will provide the production of tritium to self-sustain the fusion reaction, and covert the kinetic energy adsorbed into electricity by conventional scheme of a thermal power plant. The main breeder candidate in European project is the **eutectic Pb-16Li**. The general environment framework for the future fusion reactors, in terms of operating temperatures and radiation damage (Displacement per Atom or **dpa**) of the structural materials in shown in figure 1.
The choice of suitable structural materials for the **BB** environment remains however the main technological issue to be solved to **DEMO** deployment. In addition to high power density, high temperatures, high dose by energetic neutron spectrum **corrosion aggressiveness** and **tritium permeation** impose several and special requirements to structural materials.
Dimensional stability (in terms of void swelling, thermal and irradiation creep), adequate thermal, mechanical, and chemical properties, as well as corrosion, tritium retention and liquid metal embrittlement resistance should be guaranteed under all operating conditions. To tackle tritium permeation and corrosion attack by heavy liquid metal, an adequate protective barrier is required.
Advanced ceramic coatings, in particular **alumina** (**Al2O3**), are suitable towards this task thanks to its chemical inertia, high density and amorphous character.
In this framework, this **Ph.D.** thesis deals with the characterization and the testing under **DEMO**-relevant conditions of a corrosion resistant hydrogen permeation coating.
To meet these requirements, custom processes, namely **Pulsed Laser Deposition** (**PLD**) and **Atomic Layer Deposition** (**ALD**), is proposed according to a bottom-up approach. The main advantages of **PLD** is that it allows tailoring the structural features and mechanical properties of the coatings through **nano-scale engineering**. Previous characterization, underline an unusual ensemble of **metal-like** mechanical properties which can be explained in terms of structural features.
The characterization of the coating as hydrogen permeation barrier is performed in collaboration with C.R. ENEA (Brasimone (BO) – Italy) by means the PERI II facility. As a general statement, PLD-grown alumina (onto eurofer 97 disks of 52mm of diameter) performs effectively as permeation barrier in gaseous condition, in tests performed up to 650°C and 100mBar of hydrogen partial pressure. An unprecedented **Permeation Reduction Factor** (**PRF**) value near to 105 are obtain, with a dramatically decreasing of **Permeated flux** (**J**) of hydrogen, as shown in figure 2. By means the **diffusion-limited model** of permeation, some physical quantities such as **permeability** and **activation energy** are defined. The analyses reveal as alumina act as barrier permeation increasing, up to five time, the activation energy of couple coating-substrate (56,59 kJ mol-1) respect to the bare sample (11,4 kJ mol-1). The effectiveness of the permeation coating is evaluated in **DEMO**-relevant corrosion environment. Eurofer 97 plates are both sides covered with 1µm of PLD-grown alumina. Short test (1000h) at 550°C in saturated condition of Pb-16Li are performed at C.R. ENEA, performs effectively as a corrosion barrier. Thus, **PLD**-grown Al2O3 is a suitable and promising coating materials, as barrier, for **Nuclear Fusion** breeding blanket.
Finally, to improve the coverage of PLD-grown coating in complex geometries like **BB** and **ALD** facility is developed. In particular, ALD is developed in stop flow and optimized to grown coating onto stainless steel substrates, such as eurofer 97 samples. A first of kind thin films of the most common metal oxides namely TiO2 and Al2O3 are produced with a good adhesion and conformality in a defects and pinhole free coating.

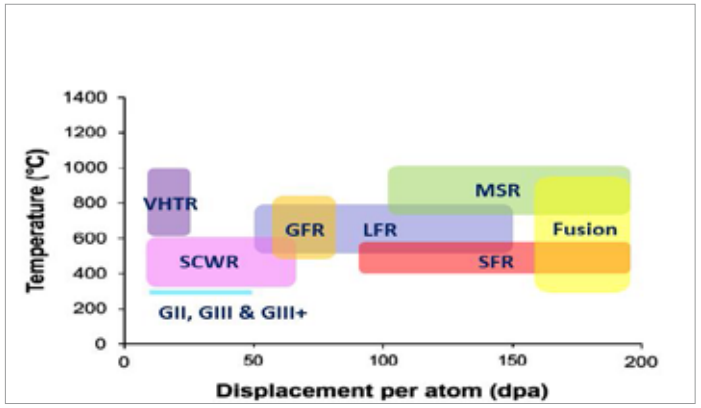

Fig. 1 - Temperature and DPA requirement for structural materials for future concept nuclear reactors. The dimensions of the rectangles define the ranges of temperature and dpa for each reactor design.

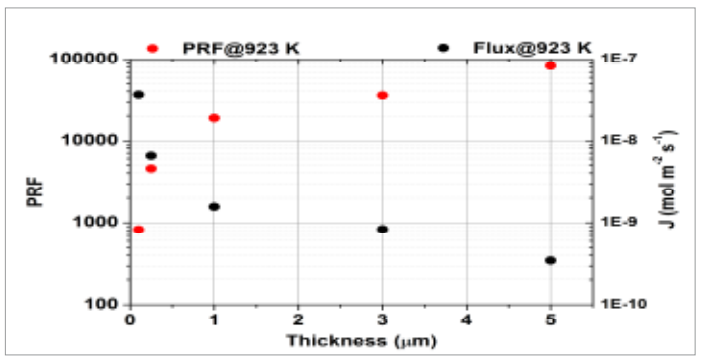

Fig.2 -PRF and J for samples coated with different thickness of alumina coating tested in PERI II at 923K.

INVESTIGATION OF ADVANCED CARBON-BASED FILMS FOR APPLICATION IN RADIATION DETECTORS

Federica Inzoli - Supervisor: Prof. Matteo Passoni

Diamond detectors are attracting great attention lately, because of their outstanding performance in harsh radiation environments such those of fusion facilities and particle accelerators for high energy physics experiments. However, their production cost competitive on a large scale is still limited by some technological issues. First, the artificial synthesis of the material, that nowadays still represents a widely investigated topic. Growing diamond is difficult, and this is even more true for the single-crystal material, that needs specific tailored process conditions in order to avoid crystallographic defects. Additionally, only few substrates can be used for single-crystal diamond deposition. Polycrystalline diamond is a relatively cheaper material, easier to be produced, having less requirements on the choice of the substrate material and deposition conditions. Particularly, polycrystalline diamond with grain size less than 100 nm (i.e. nanocrystalline diamond) are of interest for several applications (from the mechanical to the biomedical one), not just for the nuclear field. However, the lower crystalline quality influences the properties of the polycrystalline (and thus nanocrystalline) diamond-based device, resulting in worse performance. This fact widely justifies the research activity devoted to completely understand the nucleation and growth process of nanocrystalline diamond in order to produce a cheaper material (than the single-crystal one) but with a tailored structure such that outstanding properties comparable to those of a single-crystal diamond device can be obtained. Besides the material production, the other main features influencing the detector performance are i) the fabrication of optimized electrodes and ii) a complete knowledge of the device performance under irradiation, since diamond behavior in harsh radiation environments for which is thought to be employed is not well known. The main goal of this thesis is to explore all the relevant issues highlighted above. Particularly, the investigation of nanocrystalline diamond growth dynamics was carried on with an experimental approach using a direct-current micro-plasma deposition set-up: the focus was on the early stages of growth on different substrate materials, that were not pre-treated in order to investigate the growth on the native elements. Deposition parameters were optimized and a detailed characterization was performed, finding that the dynamics of the early stages of diamond growth is governed by the spontaneous deposition of a graphitic layer prior to diamond growth. Also, an experimental activity devoted to fabricate graphitic electrodes on polycrystalline diamond substrate was started. Finally, the investigation of diamond detector modifications in the crystalline structure after α and neutrons irradiations was performed, with a methodological approach aiming at introducing a characterization strategy suitable for the goal of the work. The main findings of this Ph.D thesis work are of interest for the understanding of artificial nanocrystalline diamond synthesis on different substrates, as well as useful for addressing in a methodological and rigorous way some delicate aspects influencing the device performance.

ENHANCED THERMOECONOMIC INPUT-OUTPUT ANALYSIS (TIOA) FOR ENERGY CONVERSION SYSTEM MONITORING AND DIAGNOSIS

Sajjad Keshavarzian - Supervisor: Prof. Emanuela Colombo

This dissertation is a result of three years of research in the field of *Advanced Exergy Analysis,* with particular emphasis on the following issues;

- *Input-Output benchmarking* to perform *Thermoeconomic Analysis* of the *Energy Conversion Systems.*
- *Adaptation* of the *Thermoeconomic Input-Output Analysis* method for the *Diagnosis* of energy conversion systems.
- Derivation of *stand-alone* and *reduced order Thermoeconomic Input-Output Analysis* model that can be implemented by even non-expert industrial practitioners to investigate the interdependencies between the components and performance behavior of the system during the on- and off-design working condition.

Context and motivation

Power generation is an important factor in the development of any economy. Over the past decade, gas turbines have turned out to be one of the most interesting techniques for producing electricity and being implemented in various energy intensive industrial plants. In 1990s, due to the low fuel prices, combined cycle power plants were designed for base load working condition. However, changing market conditions due to the pervasiveness of renewables, unpredictable fluctuation of fuel price, and demand reduction due to economic crises, pushed combined cycle power plants to operate in intermediate or even daily cycling mode. Cycling refers to the operation of electric generating units at variable loads, including on/off, which shortens component lifetime, increases failure rate, and raises the operation and maintenance (O&M) costs. Such additional costs make the power generation units less competitive in the liberalized power market. Therefore, it is crucial for the operators of such utilities to better understand the underlying nature of their plant O&M costs through the detailed Thermodynamic and Thermoeconomic analysis of systems, and performing proper diagnosis procedure.

There exist several methodologies to perform Thermoeconomic analysis of the energy conversion systems. These techniques, however; are debatable due to lack of solid classification as well as poor industrial orientation stem from high level of computational requirements.

This work aims to fill those gaps by benchmarking the methodologies to define and to solve the Thermoeconomic problem, and to decrease the impediments between research and practice by reducing the complexity of the Thermoeconomic analysis. To do so, two well-established benchmarks, namely, *CGAM* and *TADEUS* are employed for the purpose of description and comparison of methodologies, and to highlight strengths, weaknesses and differences among those methods. Furthermore, the issue of exergy cost reallocation of the residual flows is investigated and formalized by the aid of Input-Output method. The mathematical layout of the Input-Output method makes it suitable for such kind of analysis.

Thermoeconomic Input-Output Analysis (TIOA) method is then enhanced for the diagnosis purposes, elaborating on the specific characteristic of the Input-Output method, which investigates the interdependencies between the components. An innovative approach is proposed and formalized to identify the influence of each individual component on the malfunctioning of the other components. The new approach is called *Malfunction Decomposition* (MD) and it is applied to the well-established *CGAM* benchmark to highlight the advantages over other Thermoeconomic diagnosis methodologies. According to the state of the art provided in this thesis, most of the approaches in the field of Thermoeconomic diagnosis are aimed to localize the anomaly and to quantify the inefficiencies caused by the anomaly in terms of additional fuel consumption or economic expenses. In these cases, even if the operator detects the source of the anomaly, sometimes it is very difficult or impossible to act properly on that component during the operation of the system. Localization and quantification of the anomaly might be useful to predict the failure time or the maintenance schedule of the anomalous component. Therefore, unpredictable stoppage or failure of the system may reduce. In this thesis instead, it is rigorously demonstrated that MD can further assist the operators, providing practical information to reduce the inefficiencies causes by anomaly, once the system is operating. It provides a clear picture of malfunction structure and pinpoints the most influential component where intervention may take place to reduce the inefficiencies.

Finally, Thermoeconomic Input–Output Analysis model is proposed for the on- and off-design performance prediction of energy systems, and applied to *La Casella* Natural Gas Combined Cycle (NGCC) power plant, in Italy. The model is a stand-alone and a reduced order model, where the Thermoeconomic performance indicators are derived for on- and off-design conditions as functions of the load and of different control mechanisms, independently from the detailed Thermodynamic model. The results of the application show that the Thermoeconomic Input–Output Analysis model is a suitable tool for power plant operators, makes them capable to derive the same information as the traditional Thermoeconomic Analysis models while providing less complexity and computational effort.

Contribution of the research to the scientific advancement

Contribution of this research to the scientific advancement in the field of Thermoeconomic analysis and Thermoeconomic diagnosis of the energy conversion systems can be categorized as follows;

- *Input-Output benchmarking*. Proper method to perform the Thermoeconomic analysis of the energy conversion system has been benchmarked through the comparative application of existing methodologies on the two well-known benchmarks in the field of Thermoeconomic (CGAM and TADEUS). Moreover, the issue of exergy cost reallocation of the residual flow has been formalized for each method. Input-Output emerged as a suited and effective method to perform Thermoeconomic Analysis knowing as TIOA. It's a synthesis of Input-Output method with Exergy Cost Theory, to obtain Thermoeconomic parameters through the well-formalized approach. The straight forward mathematical structure, easiness of implementation, flexibility, and capability to investigate interdependencies between the components are the main characteristics of the Input-Output method which make it suitable for the purpose of Thermoeconomic analysis.
- *Input-Output adaptation for the Thermoeconomic diagnosis purpose.* A novel approach is developed to decompose the malfunction, taking advantage of important characteristic of Input-Output method to depict the interrelation between the components. Such decomposition enables operators or analysts to face with malfunctioning working condition with a clear picture of malfunction's structure and to minimize the inefficiencies caused by anomaly.
- *Derivation of stand-alone and reduced order TIOA model*. Application of the selected and adapted methodology on a real and complex energy conversion system provides a practical tool to be easily implemented by the practitioners to perform Thermoeconomic analysis.

FRICKE-BASED GEL FOR RADIATION THERAPY DOSIMETRY: CHARACTERIZATION AND APPLICABILITY

Giulia Maria Liosi - Supervisor: Prof. Francesca Celsa Giacobbo
Co-Supervisor: Prof. Mario Mariani

Abstract
Nowadays, an accurate and precise determination of the complete dose delivered to patients undergoing radiotherapy, i.e. the total dose to all organs from all sources of radiation treatment and imaging procedures necessary for planning and treatment verification, has acquired paramount importance. In particular, the increasing complexity of modern radiotherapy treatments has arisen the exigency to properly and accurately simulate the treatment plans in order to evaluate and minimize doses to healthy tissues and organs. Chemical gel dosimeters are promising tools to obtain experimental 3D measurement of the absorbed dose. In particular, this Ph.D. research project aims at investigating the Fricke gel dosimeters in order to attain a reproducible, accurate and sensitive tool for radiotherapy dosimetry applications. The final goal is the development of an optimized and standardized protocol, from preparation to analysis, for properly shaped phantoms to allow 3D pretreatment dosimetry. To this aim, a complete characterization and the study of the applicability for pre-treatment dosimetry were conducted.

Introduction
Fricke-based gel dosimeters are a class of chemical dosimeters composed of an acid solution of ferrous ions dispersed in a tissue equivalent gel matrix. This system relies on the dose dependent oxidation of ferrous ions into ferric ions. Thus, the ferric ions concentration is related to the total absorbed dose. The ferric ions concentration can be measured by means of both optical and MRI analysis. The optical analysis exploits the different absorption properties of ferrous and ferric ions that absorb at about 250 nm and 304 nm respectively. A dye, the Xylenol Orange (XO), was added in order to shift the ferric ions absorption from UV to Vis range, so as to allow an easier optical analysis. This ligand forms complexes with the ferric ions that mainly absorb at about 585 nm. Thus, the difference in absorbance at 585 nm is linearly related to the ferric ions concentration, and consequently to the dose, by means of proper calibration factors. The slope of the calibration curve Abs (585 nm) vs Dose defines the sensitivity of the system. The linear dymanic range of the system is about 0 – 40 Gy, so that it can be used in most of the dosimetrical application of interest in medical fields. During the last decades, a great effort has been made to develop a three-dimensional optical analysis system.
Regarding the MRI analysis, the spin-lattice relaxation rate R1 quantifies the difference in ferrous and ferric ions concentration, and thus the dose. In fact, this technique exploits the different abilities of ferrous and ferric ions in enhancing relaxation of water protons. By means of proper T1-weighted acquisition sequences, a R1-map, and thus the dose map, can be obtained.
The imaging time is a fundamental parameter in order to avoid inaccuracy in the dose map evaluation due to ferrous ions auto-oxidation and ferric ions diffusion process. In fact, despite the presence of the gel matrix and ligand, several experimental campaigns have proven that the phenomenon of Fe3+ diffusion cannot be neglected and leads to a loss of the spatial information in few hours after irradiation, especially in case of deep dose gradient. This phenomenon has to be investigated and quantified in order to avoid data misinterpretation and inaccurate dose evaluation. In order to limit the diffusion process, several solutions were developed and tested in particular changing the system chemical compositions.
To conclude, gel dosimeters present several peculiarities that make them promising for several radiotherapy applications and in particular for modern dosimetrical challenges: 3D verification of complex treatments, small-fields, edge-of-field evaluation, skin dosimetry and so on. This Ph.D. project aims at investigation the open issues in order to obtain an accurate and sensitive tool to allow 3D pretreatment dosimetry.

Experimental and Results
The Fricke-based gel reference chemical compositions have been fully characterized in order to optimize and standardize a protocol from preparation to analysis, including a proper calibration procedure. In this step, small volume samples in form of standard spectrophotometer cuvette (4.5 mL) or layers (3 mm thickness) were employed. The preparation procedures for all the compositions tested were optimized in order to obtain a reproducible system. The dosimetrical properties, such as sensitivity, dose resolution and stability (both pre- and post-irradiation) were fully characterized by means of both UV-Vis and MRI technique. In particular, a complete characterization of the MRI parameters was conducted in order to obtain a satisfactory 3D dose mapping. As result, a protocol for small volume samples from preparation to analysis – both MRI and optical – was then fully developed and characterized. These results proved to be independent on the size of the samples employed.
The dosimetrical properties and the set protocol are than specific properties of the system. Therefore, a qualitative correlation to big phantom is allowed.
As explained, an accurate evaluation of the diffusion process is fundamental. Both UV-Vis and MRI techniques were tested to assess and compare the diffusion coefficients for all the studied systems. To this aim, standard use-protocols were developed in order to allow a fast and accurate comparison of different chemical compositions.
Basic science studies were conducted in order to shine a light on the evidenced intrinsic system properties. Firstly, the reference ligand, the XO, was fully characterized highlighting some issues correlated to impurities deriving from the synthesis as well as the Fe3+ complexation mechanism, which introduces optical artifacts in the UV-Vis analysis, reported in literature and not fully described. Furthermore, the role of the gel matrix in radical production was investigated in order to extensively understand the different dose response manifested by different gel dosimeters. For this purpose, a protocol for EPR analysis was designed, thus allowing a quick comparison of the radiolytical properties of gel matrices.
Innovative compositions were designed and tested in order to overcome the evidenced limits and issues. In particular, in order to overcome the issues of both ferric ions diffusion process and the limits previously highlighted for the reference ligand XO, a novel ligand was conceived and developed. A complete characterization of the dosimetrical properties of this new system was conducted to achieve a protocol from preparation to analysis, both optical and MRI.
The diffusion coefficient was then studied thanks to the previously optimized procedures exploiting gel layers.
Finally, among the fully characterized systems, the optimal ones were chosen to be tested in specific applications. A proper phantom was developed to evaluate a SRS treatment plan, characterized by small fields. A complete protocol from preparation to MRI analysis was designed. The SRS treatment plan was developed on the CT images of the phantom. A 2D relative dosimetry was conducted with respect to a golden standard, a GafChromic film. Further investigations are still ongoing to obtained absolute 3D dosimetry.
Finally, gel layers were designed to accurately measure low doses, in particular to evaluate the skin doses absorbed during breast treatment. A use-protocol for a fast calibration was designed to accurately measure doses down to 25cGy.

Conclusions
In conclusion, the results described in this Ph.D. thesis proved the effective applicability of the Frickebased gel dosimeters to modern challenges of pretreatment dosimetry. Moreover, fundamental data were obtained to better address the future researches concerning possible chemical modifications aimed at further improving the dosimetric performance and potentiality of the system.

MULTIDIMENSIONAL SIMULATIONS OF EXTERNAL GEAR PUMPS

Javier Martínez Rubio - Supervisor: Federico Piscaglia

External gear pumps play a major role in the framework of positive displacement turbomachinery. Manufacturing simplicity and derived low cost, robustness, high volumetric efficiency and large pressure head range make external gear pumps a popular and reliable choice for a wide variety of applications. While their rigid design gives them the ability to pump high viscosity fluids in the petrochemical industry, the tight internal clearances employed in their construction make them also well suited to serve as precise flow control devices, including among others: metering applications of polymers, fuels or chemical additives. Notwithstanding their relatively simple manufacturing, operation of gear pumps involves many complex phenomena from the mechanical and from the fluid motion point of view. As a result, both numerical modeling and experimental evaluation of gear pumps have captivated the attention of many researchers in the recent years.

The numerical simulation of external gear pumps presents many difficulties from the point of view of Computational Fluid Dynamics (CFD). The thesis is focused on the complete description of the flow through 2D and 3D gear pumps, leaving behind more simplified analytical models, 1D simulations and semi-empirical methods, restricted to very particular designs and difficult to generalize. When CFD is applied to the simulation of these pumps in their full complexity, several problems arise. First of all, the extreme pressure gradients found in the liquid trapped within the chambers in the displacement phase generate significant problems in the stability and convergence of solvers. Second, no generally applicable and numerically efficient mesh motion strategy is available in literature to the best of the author knowledge, in particular when considering 3D helical gear pumps. Third, capturing the continuous flow pulsations and pressure oscillations in the different regions of the pump relays on the correct modeling of the turbulence structures in the flow. The flow through a gear pump is a clear example of a non-isotropic flow with no scale separation, some of the basic assumptions of URANS modeling, which would be otherwise the preferred choice given the complexity of the case. Overcoming these difficulties is the goal of the present thesis.

Considering the first problem, solvers convergence and derived issues are investigated for the so-called finite-volume methods, typically used in commercial CFD codes for the solution of the Navier-Stokes (NS) equations due to their simplicity and robustness. When FV methods are used with co-located grids (a very common choice) the well-known checkerboard pressure problem appears. The application of central-difference spatial discretization to the pressure gradient term in a co-located grid, produces a decoupling of pressure and velocity cell values leading to saw-tooth oscillations. This problem was addressed by Rhie-Chow using the so-called Original Momentum Interpolation Method (OMIM). However the typically required equations under-relaxation combined with the use of OMIM can generate additional problems that had not been addressed in OpenFOAM®, the main CFD code used in this thesis. Such problems include under-relaxation factor and time step size dependence of steady state solutions. When FV methods with co-located grids are used for the simulation of external gear pumps, the huge pressure gradients between adjoining lateral chambers or in the gears meshing zone accentuate the pressure-velocity decoupling and therefore the commented derived problems. The first part of the thesis focuses on the study of Momentum Interpolation Methods correcting these problems, as well as their influence on the accuracy and convergence speed of several pressure-velocity coupling algorithms, selecting the most appropriate to be used in the simulation of gear pumps.

The second critical aspect lies on the meshing process. Given the complexity of the moving boundaries in the gears meshing region and the narrow gear-to-gear and gear-to-casing gaps, mesh generation and motion is critical. The mesh replacement strategy, the most popular choice, is a very simple but difficult to control and computationally expensive method. The idea to solve this problem, described in the second part of the thesis, is to propose a new fully automatic mesh motion strategy which tries to reduce to a minimum both the computational cost and the number of parameters defined by the user, while maintaining a general approach that can be applied to spur or helical gears with any user-given profile. The method, based on a continuous deformation of a single mesh, adapts to the gears geometry in a given angle of rotation, generating a good quality mesh without the need of any mesh substitution or further user action (see Fig. 1).

Last but not least, in the simulation of the turbulent flow through a gear pump, RANS or their unsteady counterpart (URANS) would present an appropriate alternative to LES or DNS (prohibitively expensive). However, RANS does not solve for the unsteady flow structures, the intrinsic characteristic of turbulent flows, and indeed it may fail to reproduce relevant flow physics for many engineering problems. Hybrid models try to bridge the gap between the two approaches (URANS and LES) by controlling the amount of turbulent kinetic energy that is modeled. For the present thesis a new hybrid model has been developed focusing on its application to external gear pumps, leveraging the STRUCT model developed by Giancarlo Lenci. The proposed hybrid model identifies the regions where URANS assumptions lose their validity, by comparing resolved and modelled flow frequency scales. Using a *k-ε* Non Linear Eddy Viscosity Model as the base RANS, the model overcomes the need for the isotropic eddy viscosity assumption. The choice of the hybridization method, allows furthermore to identify coherent structures and regions of poor URANS performance near the rapid distortion limit, giving as a result a significant improvement with respect to the underlying RANS.

While each of the improvements can be independently applied to many other fields, the joint use of the proposed methods significantly facilitates the numerical study of external gear pumps.

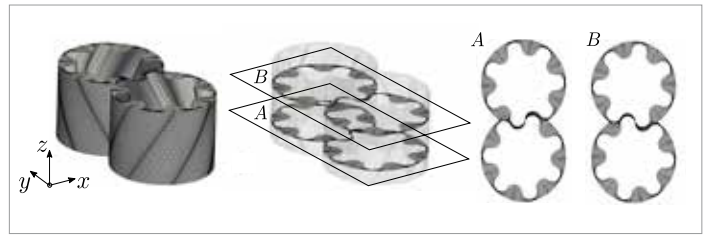

Fig. 1 - Mesh motion strategy applied to a 3D helical gear pump

HYDROGEN-TREATED TITANIUM DIOXIDE HIERARCHICAL NANOSTRUCTURES FOR WATER SPLITTING APPLICATIONS

Luca Mascaretti - Supervisors: Andrea Li Bassi, Carlo Spartaco Casari

TiO_2 is a well-known photoanode material for photoelectrochemical (PEC) water splitting, but its unsatisfactory efficiency has triggered extensive research aiming at overcoming its intrinsic limitations, such as employing nanostructured morphologies, reducing thermal treatments or the combination of TiO_2 with plasmonic noble metal nanoparticles. However, the complex defect chemistry of TiO_2 and the peculiar experimental strategy lead to challenging interpretations of the obtained results.

My Ph.D thesis work consisted in a thorough experimental investigation on TiO_2 nanostructured thin-film photoanodes with controlled properties prepared by Pulsed Laser Deposition (PLD). The major focus was related on the controlled introduction of defects with different strategies, both during the deposition process and/or the annealing one, and on their correlation with the material functional properties (evaluated with Scanning Electron Microscopy, Raman spectroscopy, optical spectroscopy) and photoelectrochemical properties (evaluated with photocurrent testing at the Laboratory of Catalysis and Catalytic Processes).

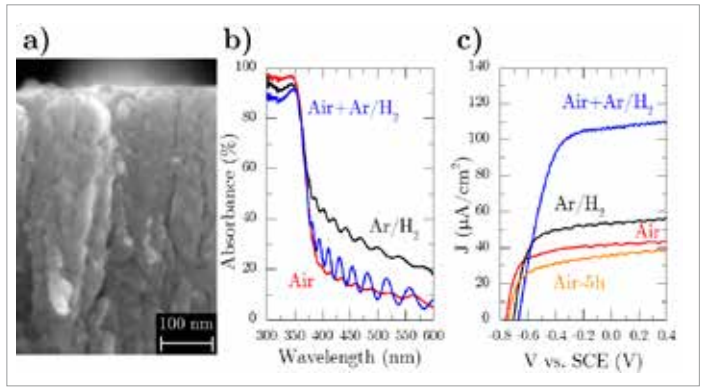

Fig.1 - a) SEM image, b) optical properties and c) photocurrent analysis of annealed TiO_2 films deposited in Ar/O_2 mixture

Also, an approach based on the integration of plasmonic nanoparticles with TiO_2 hierarchical nanostructures was developed.

The controlled introduction of defects was explored i) in the synthesis step, by employing low-oxygen content conditions (TiO_2 ablation at 5 Pa in O_2, Ar/O_2 and Ar/H_2 background gas atmospheres) and ii) in the annealing step, by combining/substituting a reference air annealing with thermal treatments in Ar/H_2 atmosphere (labeled as [Air], [Ar/H_2] and [Air+Ar/H_2] treatments). TiO_2 films deposited in pure O_2 or in Ar/O_2 atmospheres exhibited comparable morphological, structural and optical properties, while those deposited in Ar/H_2 mixture showed a more compact morphology. [Ar/H_2] and [Air+Ar/H_2] treatments did not affect the crystallization in anatase and induced a slight absorption increase in the visible range with respect to [Air] annealing. Photocurrent measurements showed that both annealing treatments and synthesis conditions affected the material photoresponse: a shortage (but not absence) of oxygen during deposition with a double thermal treatment led to clear photocurrent increase, ascribed to defects (such as oxygen vacancies) introduced in both steps, leading to better conduction or reduced recombinations.

To better understand these results and optimize the approach, a fine tuning of the oxygen content in the deposition process was addressed by employing various Ar/O_2 gas mixtures as well as Ti or TiO_2 targets. Accordingly, clear trends in photoelectrochemical results were found, showing two optimized deposition background atmosphere compositions for the double-treated photoanodes, one starting from TiO_2 target and one from Ti target, which were ascribed to optimized defect concentrations. In addition, other strategies were investigated, such as employing a second annealing step in vacuum, labeled as [Air+Vac].

On the other hand, with the aim of gaining a better understanding on the defects introduced by reducing thermal treatments, a preliminary investigation was undertaken with photoluminescence (PL) spectroscopy measurements on [Air]-, [Air+Ar/H_2]- and [Air+Vac]-annealed films with various excitation energies, both above the TiO_2 bandgap (UV) and below (visible). With visible excitations, PL emissions (peaking at orange-red wavelengths) were found only for double-treated films, possibly related to an increased defect concentration upon reducing thermal treatments.

Finally, an additional research pathway consisted in the integration of TiO_2 with plasmonic Au nanoparticles (NPs), to exploit their localized surface plasmon resonance (LSPR) to increase the material optical absorption. After developing a satisfactory control on Au NPs by controlling

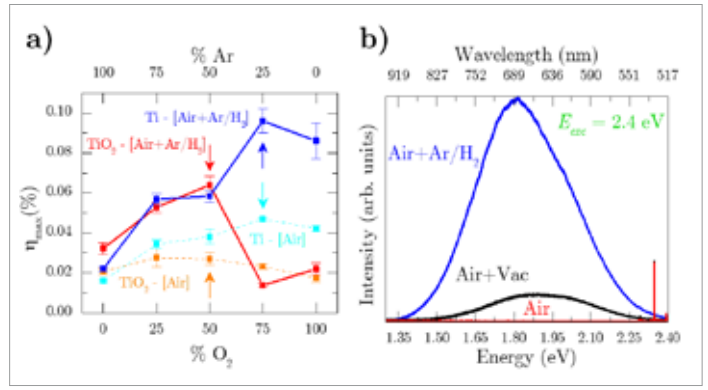

Fig.2 - a) Effect of the deposition atmosphere on the maximum photoconversion efficiency (η_{max}) for photoanodes deposited from TiO_2 and Ti targets annealed with [Air] and [Air+Ar/H_2] treatments; optimal photoanodes are marked with vertical arrows. b) Photoluminescence spectra of annealed TiO_2 films with green excitation (2.41 eV).

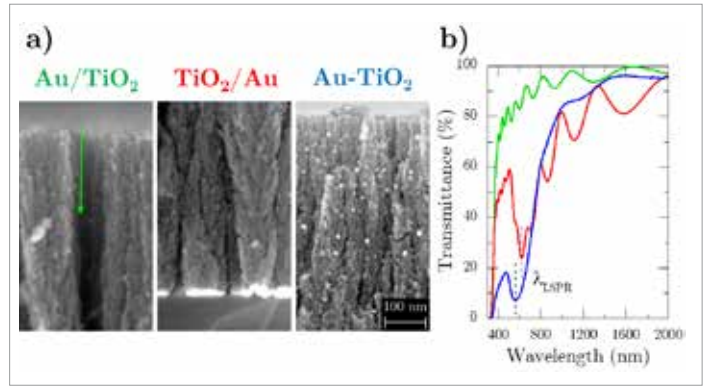

Fig. 3 - a) SEM images of Au/TiO_2, TiO_2/Au and Au-TiO_2 films. b) Transmittance spectra of the films shown in a).

PLD conditions, three different integration strategies were explored: Au on top or at the bottom of TiO_2 and co-deposition, i.e. simultaneous deposition of both materials. The latter is the most interesting approach as it enables to tune the Au-TiO_2 film composition and optical properties. Preliminary PEC testing of all films, however, suggest that an optimized composite material still needs to be obtained with further investigations.

The results presented in this thesis can provide valuable insights into the possibility to tune the photoactivity of semiconductor materials, for water splitting or other solar energy conversion applications, by controlling their properties at the meso- and nanoscale and their defect concentration.

CLEAN ENERGY CONVERSION SYSTEMS: HIGH TEMPERATURE SOLID OXIDE ELECTROCHEMICAL MEMBRANES IN ADVANCED POWER GENERATION APPLICATIONS

Luca Mastropasqua - Supervisor: Prof. Paolo Chiesa

Summary
Clean and low carbon emission energy conversion systems are considered to be one of the main ingredients to efficiently and effectively address the challenges of climate change and air quality. The power generation sector considered herein comprises a wide range of sizes and application fields, from the distributed high efficiency Combined Heat and Power (CHP) generation, to centralised generation with near zero carbon emissions, to poly-generation of H_2, electricity and heat for application into micro-grids. All these possible applications may find a successful deployment using as a common denominator high temperature electrochemical membranes based on solid oxide fast ionic conductor materials. The room for technical and performance improvement of these devices and the amount of still unexplored applications is extremely vast.
The high temperature solid oxide electrochemical membranes considered in this work are limited to Solid Oxide Fuel Cells (SOFC) and reactive Oxygen Transport Membranes (OTM). Both are reviewed for what concerns their fundamental physical and chemical phenomena which regulate their operation, including a review of the most used and promising materials. Moreover, the main applications at different scales, ranging from few kW_{el} to multi-MW power systems are discussed, highlighting the different level of maturity of both systems.

Experimental
Two testing activities focusing on SOFCs were conducted: i) a short-stack analysis; ii) a commercial micro-CHP system testing. The former work is carried out thanks to the collaboration activated between the GECOS group and the research group of Prof. Jack Brouwer at the National Fuel Cell Research Center at the University of Califronia Irvine, whilst the latter at the Laboratory of Micro-Cogeneration at Politecnico di Milano. The peculiarity of this activity is that both systems are produced by the same manufacturer (SOLIDpower S.p.a - Italy); consequently, a performance comparison of the cells operating in the two systems is possible.
The analysis on the short-stack is focused on the performance and environmental characterisation of the stack when operated with natural gas and with a syngas feed simulating an operating condition typical of Carbon Capture and Storage (CCS) operation. On the other hand, the micro-CHP system is completely characterised from a performance and environmental viewpoint at operating conditions typical of an end-user installation.

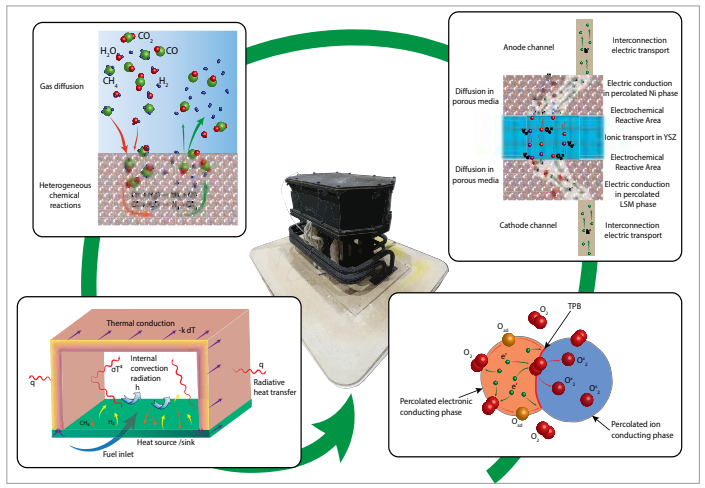

Fig.1 - Multi-scale exemplification of physical phenomena in SOFCs

Modelling
A chief contribution of this work is based on the detailed modelling activity of SOFC and OTM reactors. As far as the former one is concerned, a multi-scale model is developed with the purpose of understanding in particular how micro-structural parameters and micro-electrochemical phenomena may or may not influence the overall performance of an entire cell (see Figure 1).
The model is the result of the combined efforts with the Laboratory of Catalysis and Catalytic Processes at Politecnico di Milano.
A micro-scale model includes a description of the distributed charge transfer, the mass transport with heterogeneous chemical and electrochemical reactions, percolation theory and enthalpy balance. A macro-scale model solves the fluid-dynamic and heat-transfer models taking into account of the cell stack geometry. The model is firstly calibrated and then validated against the experimental data on the short-stack.
It is concluded that the detailed micro-electrochemistry model is able to provide additional useful insights on the design of electrodes, which in turn have important effects on the local optimisation of the cell performance. Based on these conclusions, a novel concept of "axially graded" electrodes is introduced verifying that, at least from a modelling point of view, this approach is able to increase the overall performance of a cell, at constant overall geometry of the cell layer.
As far as the modelling activity on OTM reactors is concerned, a model is built and calibrated against experimental data obtained from the literature. The model is aimed at addressing the applications of reactive OTMs either for Catalytic Partial Oxidation (CPO) or oxy-fuel purposes. The methodology proposed partially overlaps that followed for SOFCs modelling, highlighting the parallelisms between the two components in terms of physical and chemical phenomena involved and overall operating conditions.

Systems modelling
The final application of both experimental and modelling efforts of this work is focused on SOFC- and OTM-based power generation systems. In particular, three commercial SOFC systems for distributed CHP generation are analysed: i) the 2.5 kW_{el} SOLIDpower S.p.a EnGEN - 2500; ii) the 1 kW_{el} SOLIDpower S.p.a BlueGEN; iii) the 70 kW_{el} FuelCell Energy Proof-of-Concept module.
These systems are modelled by means of an in-house developed software for energy processes simulation providing the system layouts and model calibration against data obtained from the manufacturer. Moreover, for one of the considered systems, a more detailed analysis on the performance of the cells inside the system is presented employing a 2D SOFC model.
Furthermore, novel SOFC-based power system layouts are developed for both centralised (100 MW) and distributed (10 MW) generation with near-zero carbon emissions. Concerning the 100 MW-scale modelling, four novel cycles are proposed with and without CCS. These systems are studied in terms of their first and second law thermodynamic performance and a sensitivity analysis on the main SOFC operating parameters is reported. Moreover, additional systems able to increase the Carbon Capture Ratio (CCR) are suggested in order to reach the target of 90%. One of such systems envisages the combined use of SOFC and OTM reactors in series in order to perform the oxy-fuel combustion of the anode off-gas stream and allow for an efficient CO_2 capture. In this work the preliminary design of the OTM reactor is presented highlighting the efficiency improvements and land-use footprint savings possible in comparison to conventional oxy-fuel systems.
A very promising distributed generation (10 MWel) cycle with CCS is presented based on the novel concept of "electrochemical-only" CO_2 capture. The system comprises the series of an SOFC and a Molten Carbonate Fuel Cell (MCFC) in order to perform an efficient CO_2 capture and purification without the need of complex and costly cryogenic systems or big chemical islands. The system operates in poly-generation of electricity, heat and hydrogen and it is able to reach a net electric efficiency close to 70%. This result is remarkable, especially considering the application in low carbon micro-grids.
Finally, a laboratory scale test stand for H2 production in fuel cell applications is designed. The system is made up of the integration of an OTM-CPO membrane reactor with a H2 separation membrane. Herein, the preliminary design of the OTM reactor is presented verifying the possibility of an efficient integration.

DESIGN AND OPTIMIZATION OF A CROSS-FLOW INDIRECT EVAPORATIVE COOLING SYSTEM FOR DATA CENTER APPLICATIONS

Samanta Milani - Supervisor: Prof. Cesare Maria Joppolo
Co-Supervisor: Ing. Stefano De Antonellis

The PhD thesis focuses on an Indirect Evaporative Cooling (IEC) system as innovative solution to be used in confined environments as data centers. The objective of the study is the design and optimization of a cross flow air to air heat exchanger in which one of the two airflows is constantly wetted during the heat exchange process. Thus, one of the two airflows (named secondary airflow) is kept close to the saturated conditions throughout the process itself in order to increase the temperature difference between the two airflows and increase the heat transfer from the non-wetted airflow (named primary airflow). The research theme is investigated with both experimental and numerical approaches. The experimental part concerns the analysis of the performance of IEC systems in typical data centers operating conditions, to characterize the performance of the components. The numerical part focuses on the development and implementation of a model of the cooling system, starting from simplified models based on available data from existing literature and adding information coming from the experimental part on two-phase heat transfer phenomenon for different geometries, materials and humidification configurations

The study of innovative techniques for cooling systems characterized by a lower consumption of primary energy and greater efficiency is a hot topic for confined spaces such as data centers, which release a massive amount of heat through their continuous operation. The increasing number of data centers, which spread during the last decades, and the improvement of IT hardware components led to a significant increase in the power of cooling systems required to ensure equipment reliability. The electricity consumption for cooling is up to the 50% of the total energy consumption of data centers. To guarantee computers' highest performance, the indoor air should be maintained within strict ranges of temperature and humidity throughout the year independently of weather conditions and seasonal changes in temperature. Recently, guidelines for data centers widened the suggested temperature ranges according to IT equipment and achievable performance. As a consequence, the use of free-cooling extends, and indirect evaporative cooling systems become relevant to reduce the indoor temperature since they can be used in a greater number of hours during the year.

Experimental study

The experimental part provides a detailed experimental analysis of the indirect evaporative cooling system in typical working conditions of data centers. Performance of the indirect evaporative cooling system are evaluated through a test rig designed to provide primary and secondary airflows at controlled conditions (temperature, humidity ratio, and mass flow rate). Primary air conditions are kept constant in representative conditions for data center applications. Secondary air conditions are set in order to compare directly the experimental results, evaluating effects of inlet air dry bulb temperature, wet bulb temperature and humidity ratio on system performance.
To minimize the water consumption and increase the system performance, the following parameters are evaluated:
Water distribution arrangement (nozzle number, type, and flow direction);
Plenum structure and dimensions;
Water inlet positioning (i.e. from the top, from the bottom, etc);
Plate dimension;
Surface coating material.
Tests show a significant effect of water flow rate on system performance. In particular, a greater cooling effect is observed as the water flow rate increases, with little influence given by the number and type of nozzles used for the distribution of water inside the plenum.
A significant influence on the overall performance is given by the water inlet positioning, since it defines the water distribution on the plates. The best configuration to foster water evaporation all over the plate is the one that allow inserting the water from the top of the heat exchanger, as the drag force of the liquid film act in the same direction of the gravity force.
The comparison of an aluminum heat exchanger with a hydrophobic coating and one with hydrophilic coating shows the importance of surface coating material on distribution of water on the heat exchanger plate. Surfaces treated with hydrophilic coating get a more uniform water film especially at low water flow rate.

Numerical modelling

The numerical part focuses on developing, calibrating and validating a novel heat exchanger model using a finite volume approach.
A simplified model based on literature is enhanced to account for the effects and characteristics of the system observed during the experimental campaign.
A correlation to predict the saturation efficiency through the secondary air inlet plenum is obtained, in order to calculate the secondary air inlet conditions in the heat exchanger and the water flow rate entering the plates.
Then a correlation to describe the surface wettability factor (σ) is developed to link the actual system operating conditions and the non-uniform distribution of water on the heat exchanger plates ($\sigma \neq 1$). A correlation is necessary because the primary airflow outlet temperature calculated with the model and $\sigma=1$ is greatly underestimated compared to the experimental results. The wettability on the heat exchanger plates is considered as decreasing linearly in the secondary flow direction.
Part of the work concerned the optimization of the wettability factor, in order to correctly describe the heat and mass transfer phenomenon that occurs in the heat exchanger for each configuration, size of heat exchanger, and surface coating material.
The data collected during experimental tests are used to calibrate the model. The model is then widely validated in different operating conditions, within and outside the calibration range, with further tests. Numerical results show very good agreement with experimental data.

Conclusion

In the thesis, an indirect evaporative cooler for data center applications is optimized. The numerous parameters experimentally investigated, allow developing a new indirect evaporative cooling system to account for low water flow rate and high cooling performance. Moreover, the numerical model implemented and calibrated during this work, is able to predict the system behavior, taking into accounts also the effects of secondary airflow humidification as well as the surface wettability factor, as a function of working conditions and system configurations.

RADIATION-INDUCED EFFECTS ON POLYMERIC MATRICES FOR INDUSTRIAL, BIOMEDICAL AND ENVIRONMENTAL APPLICATIONS

Maddalena Negrin - Supervisor: Prof. Mario Mariani
Co-Supervisor: Dr. Elena Macerata

Plastics have successfully penetrated the global market thanks to their simple and cost-effective processing along with outstanding properties, versatility, light weight, resistance to physical aging and biological attack. Most of the conventional petrochemical-based plastics are not biodegradable and the production of ecofriendly plastics, with high degree of degradability and bio-based, is still limited by the high production costs as well as by the poorer properties. The importance of enhancing the degradability of plastic recently gained attention due to the large amount of plastic waste that goes into the environment every year and damages environmental, animal and human health. It is well known that ionizing radiations affect polymer properties and they could potentially represent an efficient strategy to affect and enhance the compostability of plastic waste.
The radiation-assisted degradation pre-treatment could be employed in an innovative, eco-efficient biotechnological approach for safely disposing the growing amount of plastic wastes occurring in landfills, terrestrial and aquatic environments, thus contributing to improve the good environmental status of the planet.
The aim of the present PhD project is to investigate morphological and nano-structural changes induced by ionizing radiation on aliphatic polymers in order to evaluate if a radiation-based pretreatment could efficiently affect the biodegradability in compost. With the objective to draw general considerations, three polymeric systems were considered, with a different rate of biodegradation: *months*, *years* and *decades*. Newly synthesized polymers that fulfill sustainability criteria have been selected as biodegradable and slow- degrading systems that are random copolymers based on Poly(butylene succinate) (PBS) and Poly(propylene cyclohexane dicarboxylate) (PPCE), respectively. Both systems have good thermal and mechanical properties that allow them to be used as eco-friendly and sustainable packaging materials. Polyethylene has been selected as a conventional synthetic non-biodegradable polymer. Since polyethylene is economic and displays an excellent stability, it is the most used conventional non-biodegradable plastic that currently accumulates into the environment.
In order to understand the overall modifications of the systems under study and to favor degradation, different irradiation conditions, in term of absorbed dose and irradiation environments, have been considered: a more reactive oxygen atmosphere, which favors degradation by oxidation, and water or hydrogen peroxide solutions, which should strongly affect the polymer surface. The simplest irradiation configuration was considered to keep the process feasible in an industrial operating gamma facility. The effects of such radiation-based treatments on the polymer properties strictly connected to the biodegradability have been studied by means of different analytical techniques. Finally, focused composting tests have been performed.

Results

The investigations performed allow deducting some general observations. According to the polymer structure, different absorbed doses or irradiation environments could be required to efficiently affect the properties that influence biodegradation. Ionizing radiation can induce modifications of the chemical structure of the polymer by the creation of radicals and oxidation products. The degradation of the molecular weight appears to be enhanced when the structure of the polymer is characterized by the presence of functional groups (*i.e.* thiodiethylene). Investigations on the biodegradable system highlighted that the introduction of sulphur atoms efficiently increases the sensibility of the system towards radiation while the introduction of the cycloaliphatic unit, as in PPCE-based systems, enabled to obtain polymers with a higher radiation resistance. The increase of surface wettability thanks to the formation of new functional groups, even in the case of slow degrading polymers, is related to an enhanced degradability. The radiation induced modifications of the crystalline fraction seem not to produce a negative effect on biodegradability.

The compostability tests evidenced that the effects induced on the degradability depend on the system stability and on the absorbed dose. As long as the stability of the system is increased, changing the irradiation environment could become determinant to significantly enhance the degradation. Oxidative environments favor degradation, in particular oxygen atmosphere and hydrogen peroxide solutions. The treatment in water efficiently affects the polymer surface leading to a better enhancement of wettability. The biodegradable copolymers showed an increased degradability even at low absorbed doses. Interestingly, a relevant difference was observed in the experiments where PBS was irradiated in water rather than in air: while PBS irradiated in air at 100 kGy resulted to be more resistant than the pristine one, PBS irradiated in water at the same absorbed dose degraded faster (Figure 1). In the case of slow degrading system, irradiation in air at 200 kGy succeeded in enhancing the rate of degradation of the copolymer films: over the same incubation period, the weight loss is about 1% for the pristine samples but increases up to the 16% when irradiated at 200 kGy. In the case of HDPE films, irradiation in air and particularly in oxygen at 200 kGy highlights a beginning of the degradation process after 180 days in compost. Disintegration tests evidenced a variation of the biodegradation rate of the treated systems, more evident as the incubation period increases. Limited to the preliminary data acquired, irradiation under specific reactive conditions seems to be effective towards biodegradation also in the case of recalcitrant polymers.

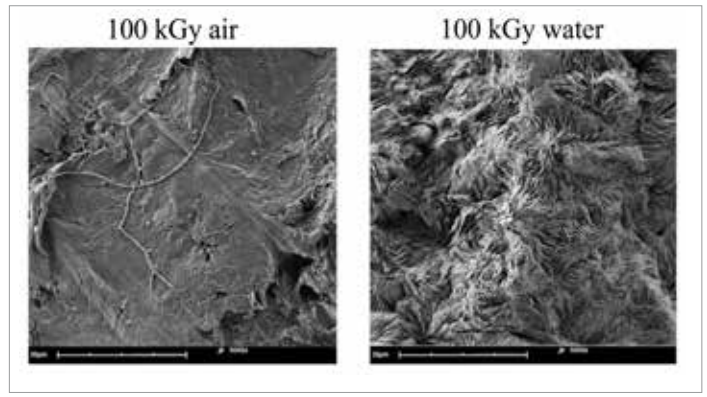

Fig.1 - SEM images of PBS irradiated at 100 kGy in air and water after 50 days in compost

Conclusions

The importance of enhancing the degradability of plastics recently gained attention due to the large amount of plastic waste that goes into the environment every year damaging environmental, animal and human health. The research work developed in the present Ph.D. project contributed to demonstrate that ionizing radiation could be a feasible potential tool to improve the biodegradability of slow-degrading plastics, environmentally-friendly and economically competitive. According to the structure of the polymer, irradiation by gamma radiation can efficiently provoke changes in those properties that strongly affect biodegradability.

CFD MODELING AND EXPERIMENTAL CHARACTERIZATION OF UREA/WATER SOLUTION INJECTION INSIDE SCR SYSTEMS OF DIESEL ENGINES

Lorenzo Nocivelli - Supervisor: Prof. Gianluca Montenegro
Co-Supervisor: Dr. Panayotis Dimopolous Eggenschwiler

Nitrogen Oxides (NOx) production is a characteristic feature of the technologies involving air temperatures higher than 1500° C, like combustion and engines. NO2 is reactive with hydrocarbons to form ozone, which can significantly deteriorate the air quality. Moreover, high NOx concentration in urban areas, which is related to more than the 40% to vehicle emissions, has a toxic potential for humans, contributing to respiratory diseases. For the current Diesel engines, Selective Catalytic Reduction of nitrogen oxides using ammonia as a reductant is an interesting solution to the NOx emission control. A safe and stable ammonia carrier is urea in water solution (UWS), which can be directly injected into the exhaust after-treatment system. The correct description of the UWS spray is the key point for a sufficient ammonia mixture preparation strategy, allowing an efficient operation of the system, its coupling with the engine over a wide range of load conditions and the reduction of the possible formation of permanent solid by-product formations on the channel walls. The focus of this work is put on the experimental investigation of commercially available pressure-driven injector behaviors in a confined environment and on the definition of numerical models to be included in a CFD platform. The experimental activity is based on optical techniques to characterize the spray evolution in cross flow conditions, and it has been carried out at Empa laboratories. The simulations are covered by the open-source 3D finite volume software OpenFOAM® which has been extended and developed to handle the phenomena involved in the system. The core of the numerical campaign involves a Lagrangian description of the dispersed phase representing the spray, coupled with a finite volume Eulerian approach for the gaseous and solid phases. Two different injectors, respectively 6 and 3 hole nozzles, operating at 9 bar with water and AdBlue® are experimentally characterized and numerically reproduced. Phase Doppler Anemometry (PDA) represents the main tool for the estimation of the spray features and shows that the six hole nozzle produces droplets with kinematic characteristics compatible with the three inclined hole ones. The influence of the urea in the liquid mixture is assessed, showing negligible variation in the nozzle operation. The PDA data are used for the initialization of a numerical model for low pressure-driven injectors to be included in the description of the dispersed phase. The Discrete Droplet Model coupled with Reynolds Averaged treatment of the gas transport equations is chosen, using the standard k − ε model to describe the turbulence. The initialization of the computational parcels mass is a key point for a reliable description of wide spray size distributions, and a new approach is proposed: a constant number of droplets is given to each parcel instead of a constant mass, producing a better simulation of the overall spray behavior. The PDA campaign is extended and coupled with previous experimental data to provide the characterization of the spray behavior in a test rig reproducing a Diesel engine exhaust after-treatment channel. The increase of momentum and temperature of the gas generates a strong entrainment of the smaller droplets (< 40 µm), which alters the full cone shape maintained at low load conditions. The effect of the urea presence is negligible, underlining that a large fraction of the liquid mass impinges the solid walls, retaining a relevant part of the water fraction. The test bench is then simulated introducing the previously defined injection model, producing a good estimation of the droplet size trends. The validated simulation of the experimental system allows the calculation of the kinematic properties of the impinging spray and the design of a mechanical patternator which is built and used to measure the planar liquid mass distribution in cross-flow conditions. Moreover, a detailed literature model is added to the CFD library to handle the spray-wall interaction, introducing a thermal threshold in the definition of the impingement regimes and improving the characterization of the secondary droplet evolution. The addition of the spray-wall heat transfer description provides the extension of the simulation to the system wall thermal transients, and the introduction of a criterion to assess of the risk of onset of liquid films. It is shown that the direct interaction between spray and the wall is the paramount source term in the overall energy balance. Eventually, a single spray pulse is simulated to characterize an injection transient when impinging on a suspended thin steel plate: a consistent temperature drop, up to 150° C, is experienced by the plate front surface in correspondence of the spray core impingement locations in each tested load condition and most of the primary interactions are destructive and represent the strongest break-up source in the system, enhancing the liquid-gas exchange surface and promoting the evaporation of the liquid mixture. The identification of the spray core location is found to be the most relevant parameter to be controlled to improve the system operation: the onset of the liquid film is strictly located in the primary impingement region, and the evaporation of the liquid is strongly dependent on the impact-induced break-up, which is necessary to reach a uniform reacting distribution at the catalyst inlet.

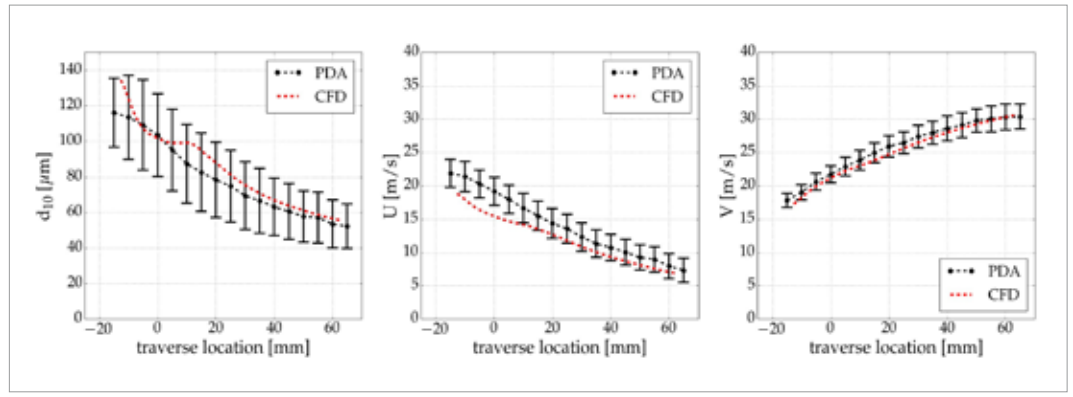

Fig.1 -

NANOSTRUCTURED TITANIUM NITRIDE BY PULSED LASER DEPOSITION AS SUPPORT FOR FUEL CELL CATALYSTS

Andrea Perego - Supervisor: Prof. Andrea Casalegno
Co-Supervisor: Dr. Fabio Di Fonzo

Fuel cell technology is by now commercially available: it is mature enough to release on the market high power devices, efficient, reliable, and it can cover a wide range of application, from stationary generation to portable applications. Automotive is the most studied field, even though also the most challenging: the main drawback of hydrogen powered cars are is in fact the economical aspect. The high costs of production, as well as the limited durability make the fuel cells not convenient with respect to cheaper and more durable solutions (e.g. internal combustion engines, batteries).
Platinum-based catalysts, which to date are the state of the art materials for electrodes are too expensive and scarce, and the development of a hydrogen based economy will raise the demand even more. Moreover, the cheap and easy to process carbon support, another key component in high performance catalyst layers, suffer from corrosion at the typical potentials and pH of a fuel cell cathode. Research is moving towards developing new materials and new electrode architectures: a whole range of non-carbonaceous supports and various supports with high surface area are studied, to grant a high dispersion of the precious catalyst (and therefore less consumption) and stability in the harsh electrode environment. Among the various candidates studied to replace carbon, Titanium Nitride (TiN), has been elected as one of the most promising for its resistance to corrosion and metal-like conductivity, that make it suitable as an electrode material. On the other hand, this material is reported to be difficult to manufacture, and requires energy intensive processes. Thanks to the possibility to control the morphology of the films at the nanoscale, Pulsed Laser Deposition (PLD) is used in this work to manufacture a TiN nanostructured support that could be able to grant a good surface area for the catalyst, maintaining the characteristic stability of TiN.

Since no literature is available on such materials, the deposition conditions were chosen to obtain a morphology that can manage the trade-off between an open porous structure and a reasonable mechanical stability. The resulting film shows a peculiar tree-like, high aspect ratio structure material has a density of 0.88 g cm^{-3} and an estimated BET area of 163 m^2g^{-1}. (**Figure 1a**). XRD pattern reveals a nanocrystalline structure, given the low signal obtained from the measurements. Scherrer analysis show a mean crystalline domain size of 7-8 nm, while from calculations of the cell parameter a loss in the nitrogen content is observed. The reason lies in the PLD process: being nitrogen the most volatile specie involved, it tends to be depleted from the material during laser ablation.

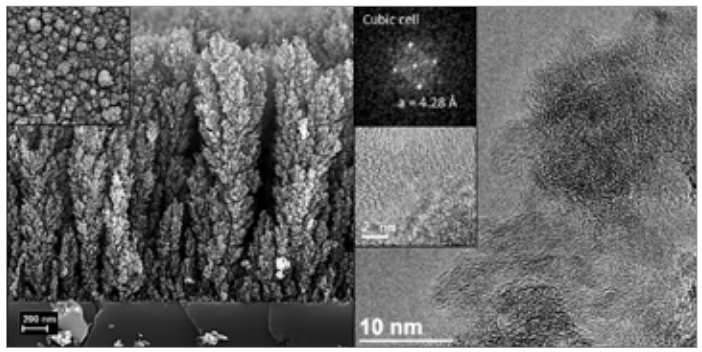

Fig. 1

Raman spectroscopy confirms the nitrogen loss by showing increased vibrational modes generated by nitrogen vacancies. It also reveals a strong affinity of the material with oxygen and its propensity to oxidation. TEM analysis confirms the nanocrystalline nature of the material and highlights the presence of an amorphous matrix in which the nanocrystals are embedded (**Figure 1b**). EDS analysis, performed together with TEM reveals the presence of oxygen throughout the material. The native oxide layer that forms on the TiN surface is enhanced by the amorphous phase therefore a strong oxygen content is found in our nanostructures.
Platinum has been deposited on the TiN nanotrees by means of pulsed electrodeposition. Pt is set to 0.3 mg cm^{-2} using ICP spectroscopy to correlate the deposited charge with Pt loading. Pt clusters assemble into high aspect ratio lamellar structures on top of the TiN scaffold, probably due to the non-uniform electric field generated by its shape.
ECSA is measured by cyclic voltammetry and is found to be around 32 m^2g^{-1} (**Figure 2a**). ORR performances are evaluated by linear sweep voltammetry. The current obtained at plateau are comparable with Pt/C E-TEK commercial catalyst, and the Tafel slope is as low as 68 mV dec^{-1}. On the other hand, the onset potential and half-wave potential are rather low, about 50 mV lower than the reference Pt/C. This could be the result of the combination of already mentioned surface oxidation and the amorphous phase that limits the electron transfer inside the structure.
Stability is also evaluated by means of specific U.S. DOE accelerated stress test protocols, aiming to evaluate the resistance to both platinum dissolution and support corrosion. With respect to the 40% target ECSA loss, platinum does not meet the requirements by only 4% difference, that can be overcome by optimizing the electrodeposition process and/or with different deposition method. On the other hand, the stability of the support is demonstrated with only a 7% ECSA loss after the specific AST. This proves that our catalyst is corrosion resistant in the harsh cell environment (**Figure 3a**). To test the PLD supports in a real fuel cell environment, a method to fabricate an actual MEA is proposed. Films coated with platinum deposited by ALD were transferred on a Nafion® 212 membrane and tested against a reference Pt/C anode (**Figure 3b**). The low proton conductivity of this configuration has been compensated with the introduction of liquid ionomer in the film by drop casting. Although the performances obtained are rather poor, as a reflection of the TiN scaffold's issues, good stability is also observed, with a 30% loss in the ECSA. The method to fabricate MEAs this way is proven to be solid, and could be a starting point for the further optimization of NSTF-based catalysts in a fuel cell environment, maintaining their characteristic structure otherwise lost during the fabrication of an ink.

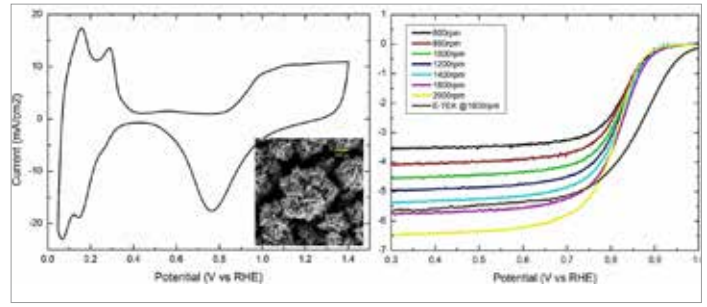

Fig. 2

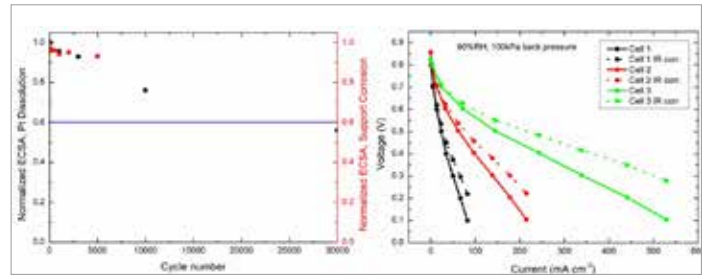

Fig. 3

ANALYTICAL AND NUMERICAL INVESTIGATION OF NATURAL CIRCULATION DYNAMICS IN PRESENCE OF DISTRIBUTED HEAT SOURCES

Alessandro Pini - Supervisor: Prof. Antonio Cammi

In case of density gradients induced by temperature differences, convective motions can arise in a fluid due to the action of the buoyancy force. Thermal-hydraulic machineries that are able to adopt this kind of flows in order to transfer heat from a hot source to a cold sink are known as natural circulation systems. Although forced convection represents a more efficient cooling strategy, natural convection does not require any active component and thus it can be used for high-reliability engineering applications. In this regard, the high-level safety requirements (which are being even more stringent after the Fukushima accident) needed in the nuclear industry have demanded research on emergency components relying on natural convection.
However, natural circulation systems can be affected by functionality-compromising dynamic oscillations of velocity, pressure and temperature fields that have to be avoided by adopting an accurate design-by-analysis approach. The onset of these instabilities can be influenced by several factors, among which the presence of distributed heat sources has not been deeply investigated in literature. Actually, this research topic is of interest not only from a scientific point of view but also for the practical instances that are characterized by distributed heating systems or involve peculiar fluids (such as exothermic reagents or nuclear liquid fuels). As for the nuclear engineering field, an example is given by the Generation IV (GEN-IV) Molten Salt Fast Reactor (MSFR), in which a molten salt simultaneously acts as fuel and coolant. In the MSFR, the heat production inside the fluid takes place through fission reactions in the reactor core and through nuclear decays of the fission products in the whole primary circuit. Such decay heat distributed along the primary circuit may modify the dynamics of a natural circulation system for the reactor cooling after the shutdown, and may lead to an undesired behaviour of the nuclear power plant, which is an occurrence that needs to be prevented. Therefore, the study of the dynamic behaviour of natural circulation with distributed heat sources, one of the key points of the EURATOM SAMOFAR Project (http://samofar.eu), is important in order to achieve high levels of passive safety, as envisaged by the guidelines of the GEN-IV Project.
In the thesis, the dynamics of natural circulation with distributed heat sources is thoroughly analysed by means of different strategies in order to highlight the several aspects that characterise this complex phenomenon. As reference natural circulation systems, single-phase Natural Circulation Loops (NCLs) are chosen. NCLs are either rectangular or toroidal loops characterised by the presence of one or more power sources, a heat sink and the pipes connecting them in such a way that they form a continuous circulation path filled with a working fluid.

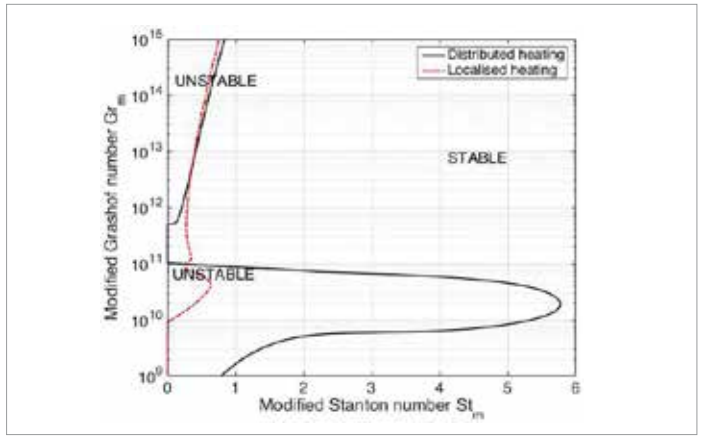

Fig. 1. Stability map of the DYNASTY facility. Unstable equilibrium points lie on the left of the transition line.

In the analysis of the dynamic behaviour of NCLs with distributed heat sources, throughout the thesis, attention is paid to the influence of the following factors: the NCL configuration; the system heat exchange features; the presence of piping-wall materials. As for the different investigation strategies that have been followed, from the linear-stability point of view, the modal analysis has been applied to evaluate the asymptotic behaviour of natural circulation systems by considering an infinite time horizon. The results of the modal approach are mainly expressed in terms of dimensionless stability maps, which are diagrams in the space of usually two parameters or dimensionless numbers, where a transition curve separates the asymptotically stable equilibria of the system from the unstable ones (Fig. 1). Differently, to take into account processes that occur on a finite-time scale, the non-modal approach has been adopted and has allowed highlighting the occurrence of the so-called "transient energy growth" also in NCLs.
Anyway, since the mentioned methods rely on the linearization process of the governing equations and give information only on the perturbation of the fluid variables, nonlinear simulations (e.g., by means of CFD) have been used as complementary approaches in order to study the actual time-dependent behaviour of the velocity, pressure and temperature inside the system. In this regard, in order to discriminate between stable and unstable operating conditions in case of numerical (but also experimental data), a stability analysis based on the information entropy approach has been developed during the Ph.D. work. Last, but not least, an experimental facility (named DYNASTY – *DYnamics of NAtural circulation for molten SalT internallY heated*) has been designed and realised during the Ph.D. work to complete the assessment of the theoretical approaches, already validated in the case of natural circulation with localised heat sources thanks to the experimental data of the L2 loop installed at the University of Genoa.
DYNASTY is a vertical square hydraulic loop (Fig. 2), made of stainless steel components, and designed in a modular way to allow future modifications and extensions. In the top part of the system, the heat sink is a finned pipe that can operate either in passive mode or coupled with an axial fan. The bottom part of the loop is branched, with each branch devised for specific experiment types. In the top one, a centrifugal pump is present in order to initialize the mass flow at system start-up, and to conduct experiments also in forced flow conditions. The bottom branch presents a flow-meter. Fiberglass electrical resistances are employed to provide the distributed external heating and can supply to the system a power from 0.5 to 10 kW. The power lines are divided into four groups, each with its own regulating system to allow for several heating set-ups. Several thermocouples are present to measure the temperature in the loop, which is thermally insulated with mineral wool material. The loop contains a molten salt as circulating fluid. The DYNASTY salt is a mixture commercially known as Hitec®, composed of $NaNO_3$ (7wt%), $NaNO_2$ (40wt%), and KNO_3 (53wt%). A tank placed at the top of the loop, which serves also as expansion volume, is used to fill the system. A second tank at the bottom is used as salt storage during the draining procedure. As for the dimensions of the system, the height and the width of the loop are equal to 3.0 m. The inner diameter of the pipe is 38.2 mm (with a thickness of 2 mm).

Fig. 2. The DYNASTY facility at the Energy Labs of Politecnico of Milano.

MODELLING AND ASSESSMENT OF INERT GAS BEHAVIOUR IN UO_2 NUCLEAR FUEL FOR TRANSIENT ANALYSIS

Davide Pizzocri - Supervisor: Prof. Lelio Luzzi

This thesis work concerns the modelling and the assessment of inert gas behaviour (IGB) in UO_2 nuclear fuel, with application to integral fuel performance codes (FPC) and emphasis on transient behaviour. The proper modelling of IGB during transients is fundamental for the performance (and safety) analysis of nuclear fuel rods, since IGB affects the thermo-mechanical condition of the fuel rods and can represent a limiting life factor for their permanence in reactor. In view of its crucial importance, IGB modelling is the main topic in several international projects. This thesis work is grafted in the FUMAC project, coordinated by the International Atomic Energy Agency (IAEA), the INSPYRE and COMBATFUEL H2020 Projects, supported by the European Commission, and the SciDAC Project on fission gas behaviour of the US DOE. For the sake of effectively and efficiently modelling IGB at the engineering scale, i.e., at the scale of FPCs (pellet and fuel rod level), it is fundamental to find a compromise between physical description of meso-scale processes concerning IGB (occurring at the scale of fuel grains) and the computational effort they impose to a fuel performance code. I adopted a modelling strategy mixed between physics-based and semi-empirical, always aiming at obtaining a conveniently simple description of IGB, suitable for FPCs. The considered IGB phenomena are:

- The evolution of the intra-granular bubble population, which can be responsible of up to half of the gaseous swelling during transients and strongly interacts with the diffusion of single gas atoms towards the grain boundaries.
- The burst release of gas occurring during temperature transients and ascribed to the micro-cracking of grain boundaries.
- The formation of the high burnup structure (HBS) with a combined description of the grain recrystallization and of the intra-granular gas depletion.

I proceeded by developing three IGB models, dedicated respectively to intra-granular, inter-granular and high burnup structure gas behaviour. Each of these models embodies peculiar physical phenomena (intra-granular bubble nucleation, intra-granular bubble coarsening, grain-boundary micro-cracking, HBS grain recrystallization) which all together allow for representing the complete evolution of inert gas behaviour during transients. This represents a significant step forward with respect to the state of art, in which some of these phenomena are represented by fully empirical correlations (with none or very limited transient capabilities) and others are completely not represented despite their potential impact on the fuel performance. I compared the results of each developed model with experimental data, according to a dedicated validation strategy (comprising uncertainty and sensitivity analyses), always showing an improvement with respect to available state-of-the-art models. In conjunction with this modelling activity, I developed two efficient numerical algorithms dedicated to the solution of specific partial differential equations (PDEs) with time-varying coefficients present in the model. In particular, the PolyPole-1 is developed for operational transients, whereas PolyPole-2 is developed for a system of PDEs overcoming quasi-stationary approaches currently used in FPCs, enabling a more representative simulation of fast transient conditions (e.g., during reactivity-initiated accidents, RIA). I verified the algorithms against a reference finite-difference algorithm in dedicated numerical experiments considering randomly generated transient histories, showing their accuracy and computational time in line with FPC requirements. Overall, the outcome of this thesis encompasses several different aspects in IGB modelling, i.e., both intra- and inter-granular behaviour, both regular fuel structure and HBS, both normal operating and transient conditions, both representation of physical phenomena and numerical aspects. All the models and the algorithms developed in this thesis have been implemented in FPCs. I personally performed the implementation in BISON (developed at Idaho National Laboratory, INL) and TRANSURANUS (developed at JRC-Karlsruhe), or directly collaborated with the code developers. Moreover, all the developed models and algorithms are available in the 0D stand-alone SCIANTIX code, developed as part of this thesis. SCIANTIX represents a POLIMI-owned software that can be included as an IGB module in existing FPCs, according to a multi-physics/multi-scale coupling strategy. In fact, in addition to providing a means for engineering calculations, thanks to their physical basis the models can be informed with parameters extracted at the smaller scales through atomistic calculations. Hence, the developed models provide an interface for scale bridging within multiscale modelling approaches. The new models are applicable with minor modifications to different fuel materials, since the main physical phenomena driving IGB are present in many fuel materials. The results shown are focused on UO_2, but extension to other materials is of future interest. For example, in the frame of a collaboration between POLIMI and INL, we are extending the present intra- and inter-granular models for application to uranium silicide fuels. Summarizing, the main outcomes of this PhD thesis are:

- The development and assessment of a physically-based IGB model (representing intra-granular, inter-granular and HBS IGB) suitable for transient analysis and applicable in FPCs. The development of numerical algorithms capable of solving the equations of the new model with computational requirements in line with FPCs.
- The development and verification of SCIANTIX, a 0D IGB code useful for testing, verification and validation of models and specifically designed for coupling with existing FPCs.
- The actual inclusion of the developed models and algorithms in FPCs, which represents a fundamental achievement from an engineering perspective.

The results obtained pave the way for further developments in several directions. A first direction is represented by the extension of the IGB model itself. As far as inert gas in oxide fuels is concerned, the extension of the work on helium is crucial (e.g., introducing in FPCs correlations for helium diffusivity and solubility in oxide fuel) due to the important role played by this gas in MOX fuels, at high burnup, and in storage conditions as well. More in general, are of sure interest the further development of the HBS model by including the HBS porosity description, the extension to other fuel materials (e.g., MOX, uranium silicide), the extension to include other non-inert fission products (e.g., caesium and iodine), the inclusion of the description of collateral physical phenomena (e.g., restructuring of MOX fuels in fast reactor conditions). Second fundamental direction is the continuation of the validation of fuel performance codes incorporating the new models against integral irradiation experiments (already performed for the inter-granular gas behaviour model). This will allow quantifying the improvement brought in using these new models. Code-to-code comparison will provide fundamental insights on code behaviour, pointing out further directions for code development. Moreover, more extensive validation is envisaged with SCIANTIX to further assess the developed models. Another fundamental direction for further research is represented by the optimization of SCIANTIX. This will lead to the development and licensing of a general tool for the development of new meso-scale models in the field of nuclear fuel performance, allowing for its use as a meso-scale IGB module in the framework of fuel performance codes.

DMFC LOCAL PERFORMANCE INVESTIGATION FOR OPTIMIZED DURABILITY

Claudio Rabissi - Supervisor: Prof. Andrea Casalegno

Undoubtedly, humankind development strictly bonds with energy technology progresses. Available, cheap and easy energy solutions are essentials feedings for global advance. In the last decades, unpreceded increasing mobility needs have been pushing energy technology towards novel solutions to meet an increasing demand for on-the-go power and energy availability. Both transportation sector, relying for around 90% on fossil fuel powered internal combustion engines (ICEs), and electronics, mostly Li-ION battery technology based, are eager of new, groundbreaking, solutions. Recently increasing global concerns for environmental compatibility, together with the awareness of them being a finite resource, fraught with geopolitical constraints and increasing costs of extraction, are strongly pushing beyond this two-century period of absolute dependence on fossil fuels. On the other side, unstoppable increasing power demands of portable electronic applications are not being met by batteries technology improvements, developing the so-called "run time gap" and growing safety issues still to be addressed.

In this scenario, among potential long-term solutions, fuel cells based on potentially renewable fuels have received considerable attention. In the transportation field, polymer electrolyte membrane fuel cells (PEMFCs) can extract significantly more power out of the same quantity of fuel when compared to traditional ICEs, thereby providing 30–90% higher efficiency (on a "well-to-wheels" basis), with absolute no environmental issues. Despite on-board storage constraints, lack of widely-developed H_2 distribution infrastructure, durability and cost issues, the commercialization of H_2-powered PEMFC vehicles has already started.

Among PEMFC technologies, immediate application of liquid-fed direct methanol fuel cell (DMFC) technology to the transportation sector is impeded by the daunting cost, limited durability and power-density issues. DMFC is more considered for markets as micro to small portable power applications, where the shorter product lifetimes and the much higher price have a lower relative importance. Actually, commercial application for DMFC technology move from micro electronics up to small industrial vehicular and portable powering applications, where long range and very short recharge times are key features, ranging from mW up to several kW of installed power per application.

Thanks to research efforts, knowledge has much improved in various fields such as catalysis, electrolytes, electrode structures, theoretical understanding of the processes and fuel cell engineering, resulting in an initial performance of DMFC nowadays acceptable for practical applications, despite several drawbacks of the technology. Unfortunately, durability and cost still remain challenging issues.

It is relatively well documented that in DMFC (even more than PEMFC) performance is the result of a complex interaction of many design, assembling and operating parameters as well as by the properties and microstructure of materials used on their construction, which are locally varying. The most important implication is an uneven electrochemical response over MEA active area, that may lead to low reactants and electrocatalyst utilization, reducing the overall efficiency and accelerating (uneven) aging of components.

Typically, literature's most diffused approach about DMFC inhomogeneous fading is to separately discuss performance distribution and uneven aging of components. While the former is investigated by means of highly locally resolved hardware, the latter relies on local post-mortem analysis, seldom correlating the results to identify determining mechanisms. Moreover, few attempts of actual optimization are present, revealing a gap between investigation and improvements development.

In this frame, the present work proposes a chronological and conceptual path starting from literature review on the field, passing through the methodology development, crossing experimental and modeling investigation, to finally lead to developing optimizations of the MEA critical components, concluding with improvement demonstration on a commercial meaningful setup.

A locally resolved experimental methodology has been appositely developed (depicted in Fig.1), combining novel RHE setup together with a macro-Segmented fuel cell hardware, permitting to spatially map electrodes potential, current density and impedance. Also, previously developed modelling platform has been properly improved to describe local performance and water distribution effects.

Investigation of local performance and degradation revealed that water distribution and heterogeneously cycling cathode potential have a strong influence on active layers' current density redistribution over time and local degradation. A novel cathode electrode, based on highly graphitized carbon support, has been selected demonstrating an increased stability under flooded conditions, leading to homogeneous material degradation. However, being local performance fading still unevenly driven by local operating limitations, cathode catalyst layer component have been locally improved through modelling optimization to ensure locally optimized operation. This lead to an in-plane gradient catalyst and ionomer loading for cathode electrode, that revealed a strong impact on local performance distribution, controllable by means of operating parameters.

As depicted in fig.2, from a comparison of 500 h degradation test, performed by means of electrochemical diagnostics together with TEM and XPS post-mortem analyses, the improved MEA demonstrated 70% lower degradation rate than the reference MEA, revealing more homogeneous operation and fading.

The results reveal a large scope for improvement obtainable pursuing a locally optimized operation and may enable improvement in overall technology development. For this reasons, the promising methodology has been finally demonstrated on a commercial-meaningful device and filed in a PCT patent.

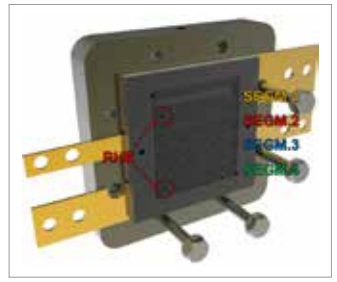

Fig.1: Rendering of macro-Segmented Fuel Cell (m-SFC) hardware, featuring segmentation in to 4 macro-regions and local mass-sampling/RHE predisposition

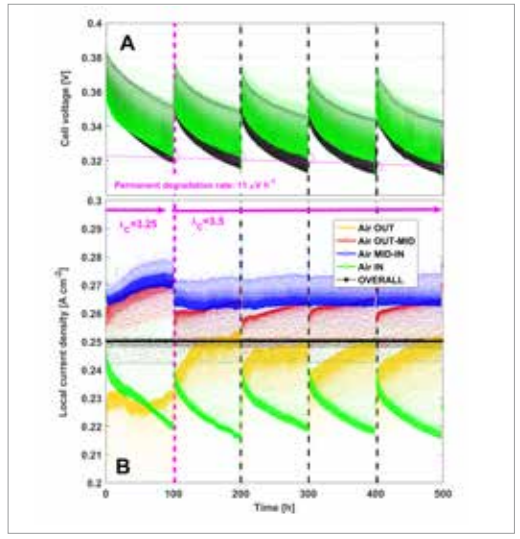

Fig. 2. Cell voltage (A) decay comparison between base MEA (black) and improved MEA (green) together with local current density (B) evolution, during a 500 h discontinuous reference degradation test performed at 0.25 A cm-2. Purple dotted line indicates operating parameter adjustment.

STUDY ON A SUBMERGED SMALL MODULAR REACTOR: INTEGRAL DESIGN, PASSIVE SAFETY STRATEGY AND CRITICAL ISSUES

Marco Santinello - Supervisor: Prof. Marco Ricotti

The theme of the thesis work concerns the investigation of an underwater Small Modular Reactor (SMR). This concept potentially offers unique safety features in terms of enhanced protection towards Fukushima-like accident scenarios, i.e. loss of off-site power and loss of ultimate heat sink, loss of coolant accident and external events. The reference concept is Flexblue (Figure 1), a 160 MW_{el} transportable and sub-sea based nuclear power unit developed by French company DCNS (now Naval Group). The plant adopts pressurized water technology and its safety relies on a passive system strategy. This concept is currently observed with interest by the nuclear community because of its innovative safety and security potentialities. The research developed during the three years of the PhD activity represents a proposal and a critical, albeit non-exhaustive, analysis of the reactor design and the potential safety features of a submerged SMR. The outcomes of the thesis can be summarized with the following key-points.

a) The submerged SMR owns safety features that inherently protect from some of the most challenging accident scenarios. The safety strategy can rely on the presence of a heat sink, i.e. the water surrounding the reactor containment, which is permanent and infinite if the reactor is immersed into the sea or in an artificial lake. The development and deployment of this concept will represent a sort of "ultimate" solution to Fukushima-like scenarios.

b) The reactor to be placed inside the submerged containment must satisfy the constraint given by the limited hull diameter and the heat transfer capability to the external water. To exploit the potentialities of the submerged concept, the reactor design must be appropriate for a fully passive safety strategy. The analysis of three proposed alternatives, i.e. VVER-type, SCOR-F and IRIS-like, has identified in the IRIS technology the most suitable design to gain compactness and to implement passive safety. A preliminary configuration has been proposed: it is a scaled version of IRIS with roughly half thermal output, where the design of primary components has been revisited to reduce the total height below 14 m.

c) A fully passive safety strategy for emergency reactor cooling has been identified, exploiting the external water as infinite heat sink. It is based on two reference processes for decay heat removal (Figure 2): (i) the natural circulation in the emergency heat removal system, if the primary circuit is intact; (ii) the long-term sump natural convection through the submerged containment, in case of a break in the primary circuit. This second process represents the ultimate solution for decay heat removal in case of failure of all the other safety systems.

d) The simulation of a station black-out scenario (intact primary circuit) and long-term cooling following a loss of coolant accident (broken primary circuit) has provided positive outcomes, predicting successful and effective decay heat removal in all the cases simulated. Simulations performed with the system code Relap5-Mod.3.3 have shown that well-designed passive system can ensure an unlimited grace period without the need of electrical inputs or human intervention.

Fig.1 - Conceptual view of Flexblue power unit

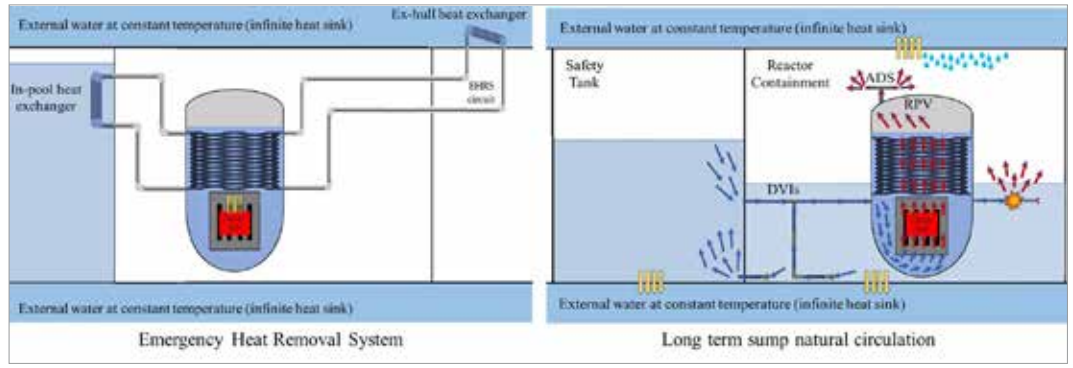

Fig. 2 - Reference scenarios of the passive safety strategy

e) A comparison with the commercial system code Apros, developed by VTT Technical Research Center of Finland, on the long-term cooling scenario has shown the same positive outcome about the effectiveness of the sump natural circulation. However, the behavior of the flow resolved by Apros is remarkably different from the Relap5 case. The analysis has provided useful elements to understand the differences at the basis of the two system codes. In particular, the preliminary investigation on a two-phase flow test case has revealed that Apros tends to overestimate the two-phase heat transfer coefficient, with respect to Relap5 and empirical correlations. This outcome seemed quite odd and has stimulated VTT to improve the two-phase modeling structure of Apros 6 code, fixing some issues in the HTC calculation.

f) An experimental testing is fundamental to assess the working principle of passive safety systems and to fill the gap of knowledge about several complex thermal-hydraulic phenomena. Two facilities have been designed in the framework of a proposal, namely INSPIRE, for the H2020 Euratom call on SMRs. The testing regards both the emergency heat Removal system and the heat transfer through the submerged containment. In addition, another experimental activity concerning an alternative configuration for the steam generator, i.e., the bayonet tube, is described.

g) Besides safety capabilities, the most relevant criticalities for the deployment of submerged SMRs have been identified and briefly discussed. The issues include (i) design of boron-free core, (ii) remote operation & control, (iii) maintenance and refueling, (iv) seismic assessment, (v) licensing procedures, (vi) international regulation, (vii) economic sustainability, (viii) public acceptance.

The findings of the thesis work about decay heat removal potentialities are very interesting and encourage further investigations to continue the development of the submerged SMR concept. The submerged concept could represent a "European" SMR proposal, in competition with US, Russian and Chinese designs. Future developments should be conducted in the framework of EU collaborations. Passive safety is a very strong point, whose benefits justify addressing the critical issues identified in the thesis. Joint efforts among industry, research centers/universities and regulatory bodies are fundamental to define the final design and achieve a valid European technology that is competitive in the global nuclear market.

SIMULATION OF INTERNAL FLOW IN FUEL INJECTION PROCESS

Ehsanallah Tahmasebi - Supervisor: Gianluca D'Errico
Co-Supervisor: Tommaso Lucchini

The role of injection system in Diesel and gasoline engines is to deliver a high quality air-fuel mixture in combustion chamber as follows efficient combustion while minimized pollutant and noise emissions. Due to the growing restrictions for emissions and energy consumption, injection process is gaining in importance. Despite the higher uncertainty and technical limitation of experimental investigations in complex systems with difficult physical conditions, numerical modeling provide a reliable results and calculate the temporal behavior of every variable at any place inside the domain.
Finding a reliable methodology for simulation of fuel flow inside Diesel and gasoline injectors is the main objective of this thesis. Considering intensive working conditions in high pressure modern injectors, including tiny dimensions, drastic pressure gradient, huge amount of velocity and turbulence properties inside the nozzle, phase changing and formation of cavitation in specific conditions make this problem more complicated.
In current research, a Homogeneous Equilibrium Model is selected and implemented for simulation of multiphase flow inside the modern injectors.

This model considers phase changing, formation of cavitation and turbulence effects in severe working conditions of real size injectors. After assessment of the approach with different experimental studies, simulation of real size industrial Diesel injectors are performed to understand the effects of working conditions and nozzle geometry on flow properties inside the nozzle and emerging sector (Figure 1). These results could be used for improvement of the simulation of spray breakup and atomization process in high-pressure Diesel sprays.
Simulation of multi-hole gasoline direct injection fuel injector (Figure 2) is another part of this thesis in which a complete realistic gasoline injector geometry, considering manufacturing tolerances is considered. Presented results for different nozzles emphasize the role of small differences in geometry on flow properties inside the nozzle and at nozzle exit sector of each nozzle (Figure 3). This difference in results consequently could affect the spray breakup of each nozzle that is interesting for further studies in future.
All the models and simulations using in this thesis are performed within the OpenFOAM technology framework and could be continued in supplementary researches in this field, as well as future works in Internal Combustion Engine (ICE) group of Politecnico di Milano.

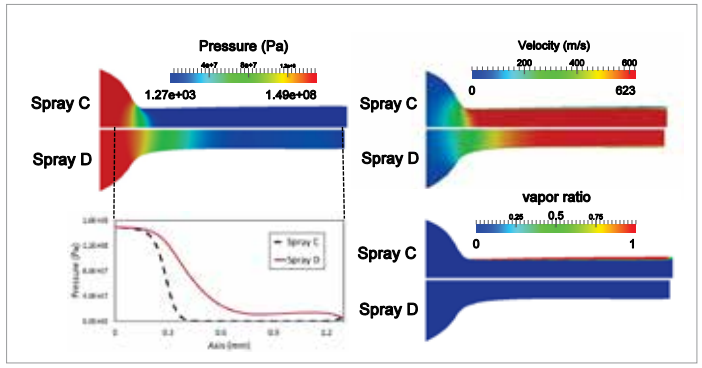

Fig.1 - Comparison of the results for two Diesel injectors (spray C and D from ECN database) with different geometry

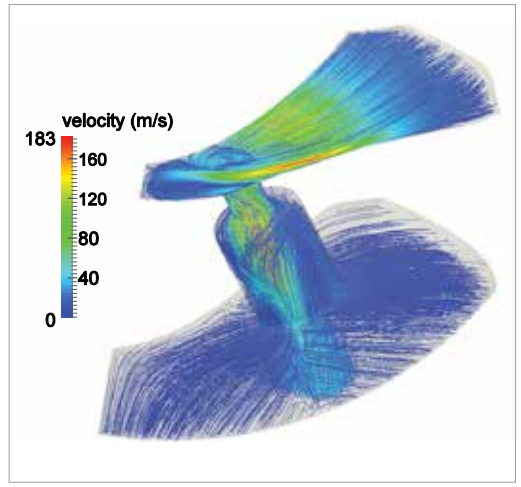

Fig.2 - Flow streamlines inside a nozzle from multi-hole gasoline injector (spray G from ECN database)

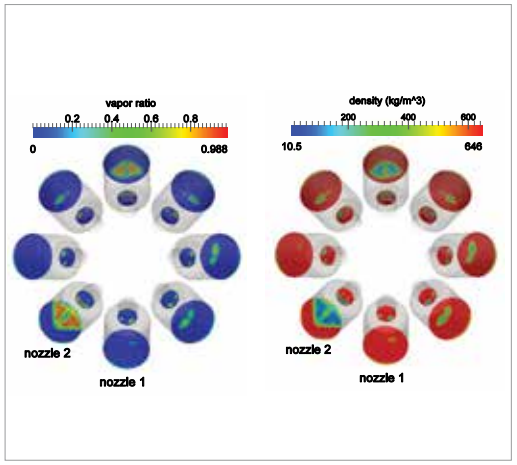

Fig. 3 - Distribution of vapor and density at nozzle exit and bore exit of multi-hole gasoline injector (spray G from ECN database)

PORE-SCALE CFD MODELING OF TIGHT ROCKS

Isabella Verri - Supervisor: Dr. Augusto Della Torre
Co-Supervisor: Prof. Gianluca Montenegro

The present research in the oil&gas field focuses on the characterization of low permeability reservoir rocks at the micro-scale by means of digital rock physics (DRP) for industrial applications. DRP is an emerging technology that allows to perform pore-scale studies combining imaging techniques and numerical modeling to simulate the flow in rock volumes.
Current challenges are addressed with the objective of extending the applicability limits of DRP.
The study is directed towards the establishment of a workflow for digital analysis that is robust, highly automatic, computationally economic. Also, the workflow shall be applicable to rock samples containing a high amount of microporosity, so that the reliability in the predictions of petrophysical data is improved with respect to the state-of-the-art.
The analyzed rock samples have experimental permeabilities in the range 0.1-100 md. Their digital 3D micro-models are obtained with a resolution of 2-4 microns by X-ray microcomputed tomography (micro-CT), a non-destructive technique for visualizing the inner rock structure. Once pores have been separated from the solid material thanks to image processing algorithms, single-phase flow is simulated across the connected pore space. Then, rock properties such as porosity and absolute permeability are predicted and values are compared to experimental data from routine core analysis.
A novel image-based mesh generation strategy has been developed and implemented in the open-source software OpenFOAM®, to create the computational grid in the pore space directly from the micro-CT images. This has simplified the problem of preserving the accuracy in the reconstruction of complex porous geometries, while saving time and resources.
Image processing and histogram-based thresholding techniques have been combined to get an automatic classification of the pore system into macroporosity, intergranular porosity and micropores. Micropores are often associated to the presence of clay materials, have characteristic sizes that are usually below one micron, play a major role in providing the connectivity of the pore system in tight rocks and are responsible for low permeabilities. Micropores are not resolved by micro-CT, and attempts in turning to nanometric resolution imaging techniques have highlighted the limitations in available computer power.
Instead, micro-scale numerical modeling allows to reproduce the fluid dynamic effects in regions of unresolved porosity without introducing further complexity in the analysis. This leads to a significant improvement in the prediction of permeability for rocks with a high amount of clays, for which computed values would otherwise overestimate experimental values up to two orders of magnitude.
In presence of unresolved porosity, two computational fluid dynamics (CFD) modeling strategies have been developed to be flexible to industrial needs, considering both the lack or the availability of higher resolution data from scanning electron microscopy (SEM).
The first model relies on micro-CT data only and describes the resistivity in the microporous regions as a linear function of the gray level of the microtomographs.
The second model is based on a multi-scale approach, where the micropermeability value applied in the micro-scale simulation is derived directly from the geometrical description of microporosity. SEM images with resolutions between 0.15-2 microns have been processed and analyzed, to statistically quantify the porosity and specific surface of the microporous phase. The coupling between the SEM and the micro-CT scale is realized entirely through an imaging workflow, avoiding complex data registration procedures in the laboratories.
Both the proposed modeling strategies have been found to be effective in improving the accuracy of permeability predictions for the analyzed rock samples. Moreover, the multiscale imaging workflow has led to a full geometrical characterization of microporosity for different rock types.