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DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Coordinator:
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The STEN PhD Program aims at providing a high level education and a challenging research experience in all the areas of Energy and Nuclear engineering sectors, facing the ambitious challenges imposed by the global priorities of sustainable development advancing global health, preserving environment and cultural heritage, mitigating the effects of climate change, efficiently exploiting energy resources and achieving decarbonization in all aspects of production, conversion, transport, distribution, storage, management and final use of energy, including urban, industrial and mobility sectors.
The PhD Programme in Energy and Nuclear Science and Technology (STEN) provides advanced scientific competences as well as complementary educational activities to develop soft and transferable skills with a multidisciplinary high-level technical knowledge and problem-solving approach in the following areas:

- production, conversion and transmission of energy
- rational use of energy and environmental control
- thermal science
- nuclear systems and nuclear fuel cycle
- radioprotection and application of ionizing radiations
- safety and reliability analysis of energy systems
- development of innovative materials for energy applications

The STEN PhD Programme is tightly related with the research activities of the Department of Energy, characterized by fundamental and applied interdisciplinary research areas in the energy and nuclear sectors. The thesis works that are presented in this Yearbook are very representative of the research activity and of some of the industrial and academic collaborations that characterize the STEN Doctoral programme.

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DATA DRIVEN FAULT DETECTION AND DIAGNOSTICS FOR HVAC SYSTEMS IN BUILDINGS

Mohammad Abdollah Fadel Abdollah - Supervisor: Rossano Scoccia
Co-Supervisor: Marcello Aprile - Tutor: Livio Mazzarella

This doctoral thesis presents significant advancements in data-driven Fault Detection and Diagnostics (FDD) specifically tailored for Heating, Ventilation, and Air Conditioning (HVAC) systems in buildings, addressing critical operational inefficiencies and energy waste prevalent in modern infrastructure. HVAC systems are essential components for maintaining optimal indoor environmental conditions, yet they are highly susceptible to operational faults including sensor errors, equipment malfunctions, control inefficiencies, and degradation due to improper or outdated maintenance strategies. Such faults often result in substantial inefficiencies that negatively impact system performance, leading to excessive energy consumption—reported to be between 15% to 30% in building systems—and increased maintenance costs, while concurrently compromising occupant comfort and indoor air quality.

In recent years, considerable progress in building automation systems (BAS), sensor technologies, advanced data analytics, and machine learning has generated increased research interest in developing and deploying data-driven FDD methodologies. These methodologies typically rely on supervised, semi-supervised, or unsupervised learning algorithms, enabling automated identification of complex fault patterns. Despite substantial research efforts, significant challenges persist, particularly in residential building contexts. Residential environments typically feature less sophisticated HVAC systems with fewer sensors and limited communication protocols, resulting in smaller datasets and fewer opportunities to capture detailed fault scenarios. Moreover, the scarcity of labelled fault data, critical for training robust supervised models, remains a primary obstacle, driven by the infrequent occurrence of faults and the high cost associated with manually inducing or annotating fault conditions.

To address these challenges comprehensively, this thesis sets out to explore three distinct yet interrelated objectives using both simulated and real-world building data.

The first objective investigates the efficacy and applicability of supervised machine learning methods for fault detection in residential HVAC systems. A residential building equipped with a hydronic HVAC system was meticulously modelled, considering realistic operational scenarios with twelve simulated faults. These faults include sensor-related issues (such as constant noise or progressive deviations) and hydronic system anomalies (valve leakages, flow rate reductions). Several supervised machine learning algorithms, namely Extreme Gradient Boosting (XGBoost), Random Forest, CatBoost, K-nearest Neighbors (KNN), and Explainable Boosting Machine (EBM), were rigorously compared. XGBoost demonstrated superior performance, achieving an accuracy of approximately 85%, balancing predictive accuracy and generalization capabilities effectively using a minimal set of easily monitored features (primarily temperature and power consumption readings). Moreover, extensive interpretability analyses utilizing the SHapley Additive exPlanations (SHAP) framework were conducted to enhance model transparency. Both global explanations, showing general feature importance, and local explanations, providing insights into individual predictions, were produced. These interpretability analyses significantly increased the practical applicability and reliability of the models.

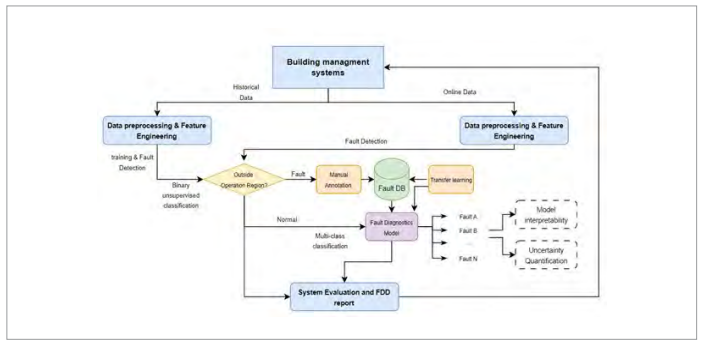

Fig.1 - Illustration of proposed FDD solution.

The second objective involves a comprehensive benchmarking of multivariate time series classification algorithms against conventional supervised learning approaches to better capture the inherent temporal patterns in HVAC system operations. Utilizing publicly available benchmark datasets tailored for FDD, the research systematically evaluated various algorithm categories including distance-based, interval-based, convolutional-based, deep learning-based, and dictionary-based methods. The deep learning-based algorithms significantly outperformed other types, attaining notable F1 scores (up to 0.92) across multiple datasets. Although the accuracy of these deep learning methods exceeded traditional techniques, their computational complexity posed practical implementation considerations. This benchmarking highlighted the importance of explicitly modelling temporal dependencies in HVAC operational data for enhanced fault detection accuracy.

The final objective introduced a novel self-supervised learning methodology designed to overcome labelled data scarcity, a prevalent challenge in HVAC FDD applications. This approach, based on a transformer architecture, effectively leverages unlabelled operational data to automatically detect subtle and evolving faults through anomaly detection techniques. A dynamic thresholding strategy, Peak Over Threshold (POT), was employed alongside the transformer-based model to dynamically adjust detection sensitivity, identifying both point anomalies (individual data points deviating from expected patterns) and sequential anomalies (extended periods of abnormal behaviour). Validation was performed using authentic operational data from a university campus building. Results confirmed that this approach successfully detected subtle faults, such as irregularities in sensor readings and scheduling issues in air handling units, without relying on prior labelling, significantly advancing practical FDD applications.

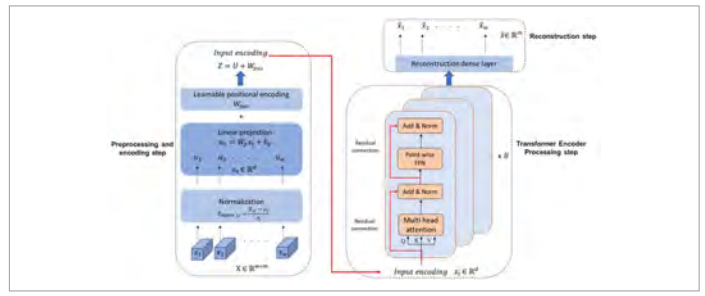

Fig.2 - On the left figure (starting from the bottom): the main architecture of the algorithm the steps of preprocessing and encoding of the data to the model dimension (d) are displayed; on the right the modelling and reconstruction of the data to the origin.

Two figures that encapsulate the thesis contributions include the schematic illustration of the integrated FDD solution framework, clearly outlining the flow from data collection, preprocessing, and unsupervised anomaly detection to manual annotation, supervised model training, and final fault diagnosis reporting. Additionally, the visualization illustrating the self-supervised model's capability to distinguish between point anomalies and sequential anomalies provided practical evidence of the effectiveness of the proposed approach.

Overall, this doctoral research provides substantial contributions to the state-of-the-art in HVAC fault diagnostics by validating supervised learning methods tailored for residential contexts, benchmarking algorithms specialized for multivariate time series analysis, and pioneering a self-supervised methodology adept at leveraging unlabelled datasets. Future research directions include enhancing diversity in datasets, further refinement of model interpretability frameworks, and advancing towards fully autonomous FDD systems capable of continuous learning and adaptation. Ultimately, these advancements support the transition towards smarter, more energy-efficient, and resilient building management practices, laying foundational groundwork for future improvements in HVAC system operation and maintenance strategies.

EROSION AND IMPURITY MIGRATION MODELLING IN LINEAR DEVICES AND TOKAMAKS

Gabriele Alberti - Supervisor: Matteo Passoni

Plasma-material interaction (PMI) is among the main challenges for the future exploitation of nuclear fusion as a reliable energy source. Both plasma and materials are affected by the interaction between these two opposite states of matter. The high particle and power fluxes expected in future devices could cause severe damage to materials, such as erosion due to e.g. physical sputtering, and morphology changes, which can influence their thermo-mechanical properties. Erosion, in turn, represents an impurity source for the plasma, thus increasing dilution and radiation cooling, potentially preventing high energy production. Finally, heavy impurities can re/co-deposit with fuel species in different locations inside the device, possibly changing surface properties of underneath materials and increasing radioactive tritium inventory. The unavoidable presence of helium (He) in plasma as a product of D-T reaction could influence and enhance these phenomena due to its peculiar interaction with materials. Being able to predict and possibly mitigate these effects is thus of paramount importance.

PMI phenomena are often studied in tokamaks. However, devices fully comparable to reactor relevant conditions are still not available and their complex environment often hinders the complete understanding of experimental dynamics. For these reasons, parallel activities in simpler experiments and the availability of modelling tools could significantly support tokamak research, with the possibility of extrapolating present findings to future devices, such as the DTT tokamak (fig.1). On the one hand, linear plasma devices (LPDs) offer a complementary and cost-effective alternative to study PMI expected in future tokamaks, exposing suitable samples to well-defined and repeatable plasma conditions. On the other one, the 3D Monte-Carlo code ERO2.0 is widely recognized as state-of-the-art for erosion and impurity migration studies.

The main goal of this PhD thesis thus consists in supporting the interpretation of experiments carried out in LPDs and tokamaks by means of ERO2.0 modelling, eventually exploiting the acquired experience to make reliable predictions for DTT design.

For this purpose, erosion and impurity migration phenomena are studied in different devices, from the microscale to machine-scale global simulations.

Tungsten (W) coatings with different morphology (fig.2) have been deposited on substrates with different roughness and exposed to He plasma in the linear device GyM, to study topography effect on sample erosion. The microscale topography of exposed samples has also been directly imported in ERO2.0 simulations for comparison. Both experiments and simulations agree in identifying the mean surface inclination angle as a better descriptor of sputtering yield variation with respect to roughness. SOLPS-ITER and ERO2.0 codes have been coupled for the first time in linear geometry to perform global modelling of wall erosion and transport in GyM. Wall eroded impurities are shown to contribute to sample erosion in range 15 – 20% for impact He energy in proximity of the sputtering threshold.

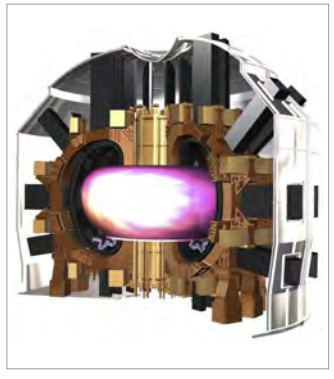

Fig. 1 - Schematic view of the DTT tokamak.

ERO2.0 modelling has also been applied in tokamak geometry to support experiment interpretation in AUG D and He plasma discharges. In the former case, global modelling of first wall erosion and transport to the divertor region shows that wall eroded W could contribute to gold marker erosion in range 5–15% according to free simulation parameters, while it drops below 1% for Mo ones. In He discharges, the role of He ion concentration on divertor erosion has been studied by means of a simple analytical model and with ERO2.0, showing the dominance of He^{2+} erosion in this plasma temperature regime. A good agreement is found with experimental data, considering a variation of plasma parameters within their uncertainty and including a reasonable presence of light impurities in plasma.

Finally, SOLPS-ITER and ERO2.0 W density predictions in plasma have been compared, highlighting advantages and limitations of the two models.

This experience has been exploited to provide first indications for DTT design. Two lower single-null scenarios have been investigated, i.e. attached plasma in pure D and detached with Ne seeding, with the aim of assessing the erosion/deposition pattern and W core contamination from the divertor region. A comparable peak erosion is observed in the two scenarios in ELM-free conditions, while net erosion is found to be overall dominated by ELMs. W core contamination is observed to stay below acceptable limits in all the investigated scenarios (fig.3). The horizontal flat parts of both targets and the central flat part of the dome are identified as the least screened areas of DTT divertor, which could raise concerns in case of a W source there. Thanks to the comparison with WEST experience, the DTT good screening properties are ascribed to a combination of closed divertor geometry and to the high electron density near surface.

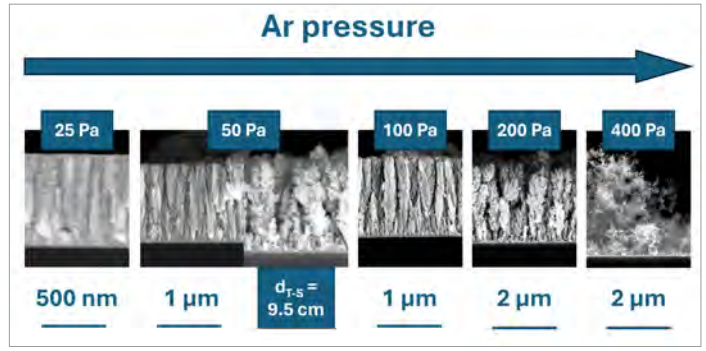

Fig. 2 - Cross-section scanning electron microscopy (SEM) view of tungsten coatings deposited via pulsed laser deposition as function of the background argon (Ar) pressure.

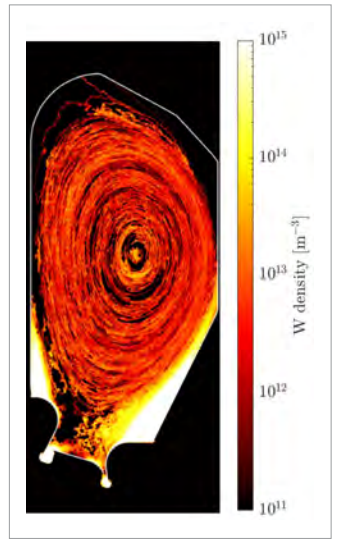

Fig. 3 - 2D poloidal density of tungsten eroded from the divertor region in the DTT tokamak during ELMy scenario.

OPERATION AND MAINTENANCE PLANNING OF CONCENTRATED SOLAR THERMAL TOWER PLANTS: SOILING MITIGATION AND RECEIVER CONTROL

Cody Blain Anderson – Supervisors: Giampaolo Manzolini, Michael Cholette, Giovanni Picotti, Darren Pearce

Tutor: Paolo Chiesa

Concentrated solar power (CSP) is a promising technology that can be used to harness and store dispatchable thermal power. Yet, CSP has a high cost of electricity, due partly to its high operation and maintenance (O&M) cost. One of the key cost drivers for CSP O&M is the soiling of the heliostats in the solar field, where accumulated dust diminishes the field reflectance and thus overall productivity of the plant (see Figure 1). While this loss can be mostly recovered via cleaning operations, the trucks, personnel, and resource use (e.g. water) is considerable and must be carefully balanced against productivity gains. Yet, tools for modelling and implementing this balance are either lacking or incomplete. Existing soiling models omit key phenomena (e.g. moisture effects on soil deposition / adhesion) and cleaning optimisation studies assume that artificial cleaning reflectance recovery is perfect and neglect the possibility of mixing cleaning technologies to further reduce overall costs. Therefore, the aim of this thesis was to develop methods to characterise soiling processes and optimise the cleaning resources for real CSP sites. The developed tools and analysis have been employed to reduce O&M costs for solar tower technologies and improve the performance of solar tower technologies.

The impact of wet soiling phenomena on the optical characteristics of solar collectors is considerable; however, there exists a limited body of research addressing the influence of dew on optical measurements. Through experiments, this project investigated how condensation interacts with pre-soiling and post-soiling stages via analysis of soiled mirror mass, reflectance and microscopy. The soiling and condensation cycle can be characterized by four primary phases (highlighted in Figure 2): initial dry homogenous soiling pattern, nucleation of water condensation pushing small particles, coalescence of water droplets pushing larger particles towards the edges of the newly formed droplets, and finally, the evaporation of dew around the largest particles, resulting in a honeycomb agglomerated soiling structure. The study utilised Gaussian mixture models and multivariate linear records to correlate the effect of mirror tilt angle, airborne dust concentration, and condensation amount on particle size distribution and reflectance. While condensation had minimal impact on particle deposition, it significantly influenced reflectance of pre-soiled mirrors, especially at high tilt angles (70°), where up to a 6% points of reflectance improvement was observed, whereas lower tilts led to a degrading of mirror reflectance for the same levels of soiling.

Fig.1 - Operator Comparing Reflectance of a Soiled (left panel) and Clean (right panel) Heliostat within a Central Tower Receiver Field

This project also led to the development of a soiling prediction and cleaning resource methodology (shown in Figure 3) to optimize cleaning strategies for a prospective 50 MW CSP+TES plant in Mount Isa, Australia during its early design phase. By calibrating a dry deposition soiling model with site-specific meteorological measurements, predicted soiling rates informed cleaning schedules, minimizing financial uncertainty of operation and maintenance staffing and asset needs.

The base case scenario, using vertically stowed heliostats, required two cleaning crews for 24 field cleaning rotations annually. Alternatively, heliostats can be stowed horizontally at night to reduce wind loads and corrective re-alignment maintenance. Although this subjects the heliostat to increased soiling losses by 114% with respect to a vertical stow and raises plant production losses and cleaning costs by 51%. A comparison of cleaning technologies revealed that although deluge-style cleaning was faster, its lower cleaning efficiency raised O&M cleaning costs by 275%. An autonomous electric cleaning vehicle demonstrated a 61% cost reduction to the base scenario due to lower consumables and labor costs. Finally, field design optimizations showed that reducing heliostat field size increased cleaning rotation speed, while larger fields reduced the need for pristine cleanliness due to receiver flux saturation limits.

This project provides key tools and analyses to reduce O&M costs in CSP tower plants. The findings highlight how moisture affects solar collector cleanliness and how O&M and design policies influence cleaning efficiency and costs. These insights offer valuable guidance for optimizing O&M strategies across different CSP configurations.

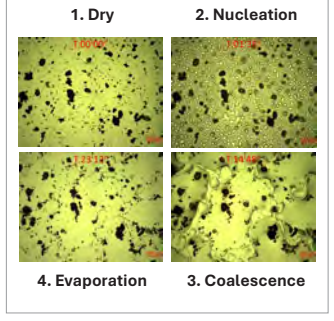

Fig.2 - Bright-Field Microscopy of Condensation Growth Phases. 1) Dry Mirror with soiled black particles. 2) Initiation of water growth, 3) Joining of water droplets, 4. Evaporation of condensation leaving a new reflectance altering soiling structure.

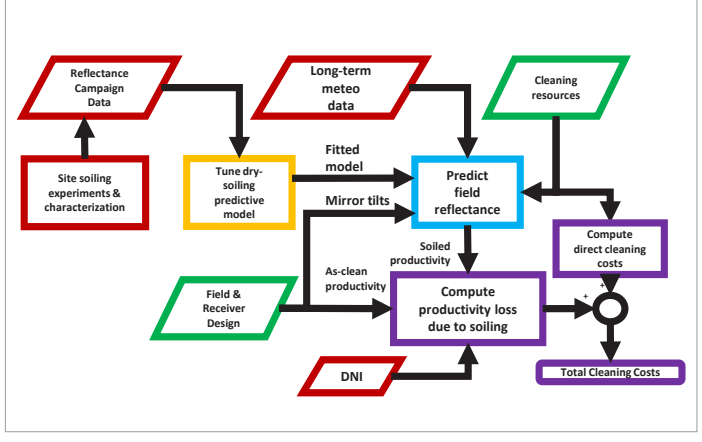

Fig. 3 - Site Soiling Characterization and Cleaning Asset Optimization Methodology

TAILORING MECHANICAL BEHAVIOR OF METALLIC THIN FILMS THROUGH NANOENGINEERING DESIGN STRATEGIES: INVESTIGATION OF METALLIC GLASS AND HIGH ENTROPY ALLOY FILMS

Francesco Bignoli - Supervisors: Damien Faurie, Andrea Li Bassi, Matteo Ghidelli

The study of mechanical behavior of metallic thin films has become increasingly important for many applications in the field of high resistance coatings, stretchable electronics, memory storage and aerospace. Moreover, experimental observations have shown the activation of mechanical size effects, increasing the yield strength (σ_y) and delaying the mechanical failure of micrometric sized samples. This has opened new approaches in the research of high-performance metallic materials and structures with better mechanical performances.
One class of materials which drive researcher activities are metallic glasses (MGs), or amorphous metals, which are characterized by absence of long-range order and defects typical of crystalline metals (i.e. dislocations and grain boundaries), which confers them unique mechanical properties such as high σ_y (> 2 GPa) and elastic deformation (2%). However, they show limited plasticity due to their inherent brittleness caused by nucleation and the catastrophic propagation of shear bands (SBs). Yet, the transition from bulk to thin films form allows to trigger size effects, improving their plasticity by preventing the nucleation of SBs, due to geometrical confinement.

A second emerging class of metallic materials are the compositionally complex alloys also known as high entropy alloys (HEAs). Discovered in the late 1990s independently by the groups of Cantor and Yeh these alloys are obtained by mixing four or more metallic elements in equiatomic concentration, obtaining a single-phase crystalline structure with a heavily distorted lattice due to the presence of multiple elements with different atomic radii. Unlike conventional crystalline alloys, such atomic structure results in high strength which is maintained even under sever mechanical solicitations and/or high temperature environments (i.e σy ~0.7 GPa at 1000 °C for NbCrMoTaTiZr). However, most of the studies on HEAs are based on bulk samples, while the investigation of HEA thin films (TFHEAs) has gained interest only recently, due to a better control of the microstructure, grain size and the avoidance of the intergranular segregation of elements and chemical gradients as observed in the comparison of the microstructures of cast and sputtered CoCrCuFeNi alloys. Nevertheless, for both TFMGs and TFHEAs, the lack of understanding the exact relationship between micro- and nanostructure and mechanical behavior hinder the possibility to develop thin films with improved mechanical properties and it is representing an open field for research. In this field different nanoengineering strategies are being studied in parallel to improve the mechanical properties such as interface engineering through cluster-assembled growth to introduce local density and chemical gradients to mitigate localized deformation phenomena. A second strategy is the coupling of amorphous and crystalline materials in multilayered structures to increase the overall strength and plasticity of the film thanks to the presence of interfaces which confine the movement of dislocations and SBs avoiding brittle failures.
In this context, the objective of this project was the synthesis of nanoengineered TFMGs and TFHEAs by exploiting the versatility of Pulsed Laser Deposition (PLD), while investigating the interplay with structure and mechanical properties, exploiting a panel of characterization techniques ranging from SEM, XRD and TEM for the structure to Brillouin light scattering and *in situ* SEM micropillar compression for the mechanical properties.

Specifically, a wide range of controlled nanostructures have been deposited, i.e. compact and cluster-assembled (nanogranular) monolithic $Zr_{50}Cu_{50}$ and $Zr_{46}Cu_{46}Al_8$ TFMGs to improve plasticity.
Moreover, a large part of the PhD work consisted in the synthesis of crystalline/amorphous ultra-fine (9/4 nm) $Zr_{50}Cu_{50}$/Al nanolaminates whose high number of interfaces can block SBs propagation, greatly improving their strength and plasticity.
Finally, oxygen incorporation has been investigated with the synthesis of dual-phase amorphous oxide-metal glasses $Zr_{50}Cu_{50}$/O and $Zr_{46}Cu_{46}Al_8$/O were deposited which are able to deform homogeneously due to the free volume associated with covalent O bonds to fully suppress localized plastic behavior.
CoCrCuFeNi TFHEAs were deposited with controlled crystalline orientation and grain size to trigger strengthening mechanisms such as Hall-Petch strengthening.
PLD compact $Zr_{50}Cu_{50}$ and $Zr_{46}Cu_{46}Al_8$ have similar σ_y values of 2.8–3 GPa and homogeneous deformations up to 4%. These values are much higher than the σ_y (2-2.5 GPa) and homogeneous deformations (2-3%) found in literature for conventional TFMGs thanks to the larger density related to the high kinetic energy of the ablated species, leading to improved elastic and plastic properties. The transition from compact to nanogranular PLD TFMGs increases the homogeneous deformation achievable before SB propagation, reaching values up to 6.7%. This is possible thanks to the larger amount of free volume present in the nanogranular structure with respect to the compact one, preventing the maturation of a single big SB and instead creating multiple small SBs and promoting a less localized deformation. These properties are kept for large specimens > 1.3 µm diameter well above the sizes for which mechanical size effects are activated for MGs (< 0.5 µm) indicating that PLD nanostructuring is able to extend the range of activation of mechanical size effects.
The incorporation of O in the PLD films further increases both the σ_y and homogeneous deformation with compact $Zr_{50}Cu_{50}$/O and $Zr_{46}Cu_{46}Al_8$/O reaching values ~4.5 GPa and deformation values up to 6%. The transition from compact to nanogranular dual phase glasses drastically increases the plasticity of the PLD films, reaching homogeneous deformation values > 15% without formation of SBs, while keeping σ_y ~4.4 GPa due to the combination of the nanogranular morphology and the structure of O-rich and Cu-rich phases, which results in large amounts of free volume able to suppress SB formation.
The presence of interfaces in (9/4 nm) $Zr_{50}Cu_{50}$/Al nanolaminates confining and deviating the SBs in the amorphous layers improves the plasticity of compact nanolaminates with respect to compact $Zr_{50}Cu_{50}$ counterparts (3.6% vs 3%), while keeping high σ_y ~3.6 GPa. Most importantly the nanogranular nanolaminates prevent the propagation of mature SB events thanks to the combination of the inter-layer chemical heterogeneities and the intra-layer density fluctuations related to the cluster assembled growth, developing only superficial non percolative SBs even for deformations >15%.
The study of CoCrCuFeNi TFHEAs deposited by PLD has yielded great results showing that it is possible to control the crystalline structure by changing the deposition pressure thus tuning the grain size, texturization and crystallite growth direction. This allows to control the strength and the plasticity of the PLD films and the smaller grain size of PLD CoCrCuFeNi with respect to its sputtered counterparts confers to PLD CoCrCuFeNi larger hardness. PLD CoCrCuFeNi has also demonstrated remarkable ductility in tension when coupled with a polymer substrate, reaching crack onset strains up to 3.44% combined with large toughness and film – substrate adhesion with respect to sputtered counterparts,
Overall, within this PhD thesis we open the way to the use of PLD as a new technique to synthetize metallic films with unique nanostructure and composition leading to tailored mechanical properties with potential for various applications as high-performance structural coatings.

PASSIVE NEUTRON DOSIMETRY WITH PADC TRACK DETECTORS – NOVEL APPLICATIONS AND OPTIMIZATION OF INDIVIDUAL MONITORING

Matteo Bolzonella – Supervisor: Marco Caresana

Track detectors made of PADC (poly allyl diglycol carbonate, also known as CR-39) are among the most effective instruments available to perform neutron dosimetry, as demonstrated by their widespread adoption among individual monitoring services (IMSs) and the sustained interest in research studies on these devices.
This work contributes to the enhancement of passive neutron dosimetry with PADC track detectors by (1) improving the signal analysis methods, (2) extending the applications of these instruments to novel and/or challenging situations, and (3) performing studies to improve the detector material.
Concerning the first point, the major achievement is the development of a novel track discrimination method based on a genetic algorithm for fast neutron dosimetry using the *Politrack*® system – an automated reader for scanning and analyzing PADC detectors. The approach is illustrated in **Figure 1**. The input of the algorithm consists of two files which basically contain actual tracks and background objects, obtained by scanning a set of reference detectors irradiated with a calibration AmBe neutron source and a set of unirradiated detectors, respectively. Then, the algorithm mimics natural selection using the genetic algorithm of the *MATLAB*® code to find the best extrema (i.e., lower and upper thresholds) for seven selected track parameters, which act as filters for track discrimination, in order to preserve as much signal as possible ($S_{\%}$) while minimizing the background ($B_{\%}$). This approach enhances the signal-to-noise ratio (intended as the average number of tracks for a given neutron dose divided by the average number of background tracks) of PADC-based fast neutron dosimetry by a factor of approximately 2 compared to the standard track discrimination method of the *Politrack*® reader.
As for the second point, a fast neutron dosimeter built by coupling a PADC detector with a 1-cm-thick PMMA radiator and based on LET spectrometry was characterized through experiments and Monte Carlo simulations (using the *FLUKA* code) in a variety of situations of practical interest. The results indicate that the dosimeter has a rather flat response function over a wide energy and angular range (**Figure 2**) and demonstrate that it is suitable for use in stray neutron fields with neutron energies up to about 1 GeV, typical of high-energy particle accelerators. Furthermore, a rem counter based on PADC detectors coupled with boron converters (*passive LINUS*), upgraded using new converters highly enriched in B-10 and an algorithm to correct for track superposition similar to the dead-time correction method used for gaseous counters, was tested with experiments and benchmark studies, showing that it can be effectively used for area monitoring in facilities generating intense and/or pulsed neutron fields, such as those produced by recent/emerging technologies like laser-driven particle acceleration and FLASH therapy.
In addition, PADC detectors coupled with B-10 films were employed to assess neutron contamination in X-ray radiotherapy treatments delivered by high-energy LINACs (i.e., using accelerating potentials > 10 MV), which is particularly concerning for patients with cardiac implantable electronic devices (CIEDs). Experimental data and a Monte Carlo model for the *MCNP* code confirmed that these instruments enable precise measurements useful for risk assessment.
Finally, the third point is addressed through the *CR-39 Quality* task of EURADOS (European Radiation Dosimetry Group), led by the Politecnico di Milano. The task, which is an action of the EURADOS Working Group 2 – *Harmonisation of individual monitoring* (WG2), is conceived as a close international collaboration among researchers, IMSs and PADC manufacturers to improve and harmonise neutron dosimetry with CR-39. Although the task is a long-term project, it has already reached significant milestones, including the publication of an updated review paper on the state of the art of neutron dosimetry with PADC, which shares best practices contributing to the standardization of this discipline, and carrying out an experimental campaign to characterize various currently available PADC materials, providing valuable insights to enhance the quality and, consequently, the performance of the PADC material used for neutron dosimetry.
As a final remark, it is worth mentioning that the activities carried out in this PhD project contribute to the advancement of neutron dosimetry techniques and instrumentation, in line with the latest edition of the EURADOS Strategic Research Agenda, which identifies the most important future research needs in radiation dosimetry in Europe based on inputs from the EURADOS Working Groups and stakeholders.

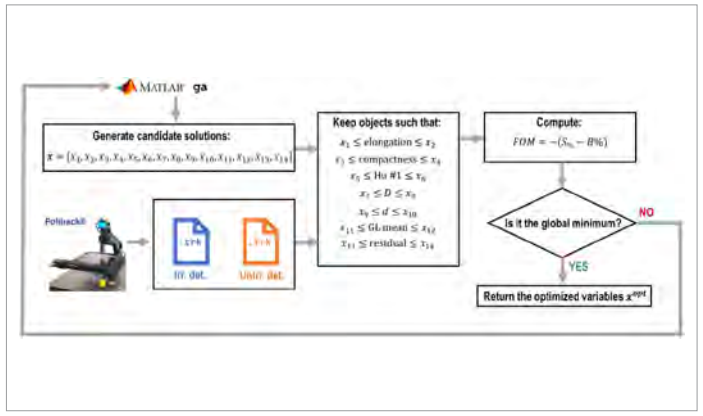

Fig. 1 - Schematic representation of the new track discrimination method for fast neutron dosimetry using the *Politrack*® system.

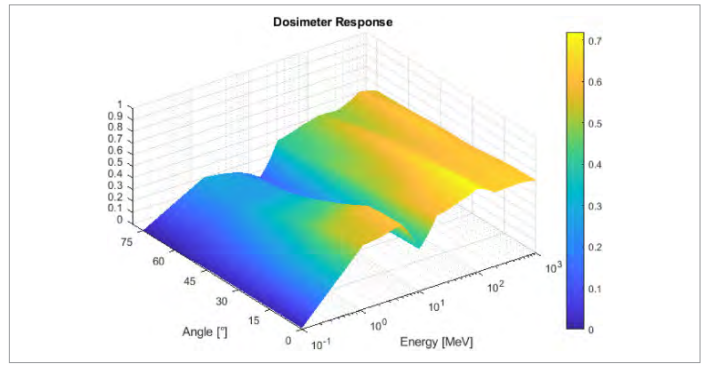

Fig. 2 - Response function of the dosimeter in terms of personal dose equivalent Hp(10) as a function of energy and angle of the impinging neutron field. The response is defined as the ratio between the instrument reading and the actual Hp(10) value. A similar trend is observed for the response in terms of ambient dose equivalent H*(10).

NOVEL TECHNOLOGIES FOR GREEN AMMONIA UTILIZATION AND PRODUCTION FOR CLEAN POWER GENERATION

Alberto Cammarata - Supervisor: Stefano Campanari

Tutor: Paolo Colbertaldo

Introduction

The conversion of fossil fuels to foster economic growth is widely considered the root cause of climate change. Moreover, the uneven geographic distribution of fossil fuels causes wars and disputes due to the prospects of wealth and power. Renewable energy is a solution to these issues, allowing for a more decentralized energy system where each country can provide for its own energy needs. The key technical challenge to realize this vision is to deal with the intrinsic uncontrollability and intermittency of Variable Renewable Energy (VRE) sources in an economically viable fashion.
In this framework, storing renewable energy for later use is both an essential and challenging solution. In particular, chemical storage is a promising option for long-duration energy storage and long-distance transport of clean energy, mainly due to the high volumetric energy density that can be achieved.
Green H_2 is considered the benchmark solution for chemical storage of renewable energy. However, other fuels have been proposed for this purpose. Ammonia (NH_3) is one of these fuels, and its main advantages are larger volumetric energy density compared to liquid H_2, a well-developed infrastructure, the possibility of liquid storage at relatively low pressure, and the fact that it does not emit CO_2 upon utilization. If ammonia is produced from electrolytic H_2, then only H_2O and N_2 are required for ammonia production. Moreover, most literature works highlight that ammonia is a better energy carrier compared to liquid H_2 for long-distance shipping of clean energy, at least from an economic perspective.
In order to use NH_3 as a clean fuel, it is necessary to develop technologies for its utilization for power generation, and for its production using renewable electricity. In the last decade, the research on both these aspects has been intensifying, since the benefits of using ammonia have been increasingly recognized.
This thesis adds a contribution to these topics, investigating by means of thermodynamic simulations two innovative power generation systems using ammonia as fuel, and an innovative plant for NH_3 production using electricity.
The innovative systems proposed share the use of high-temperature electrochemical devices, like Solid Oxide Fuel Cells (SOFCs), Solid Oxide Electrolysis Cells (SOECs), and Oxygen Transport Membranes (OTMs), in order to maximize their energy conversion efficiency.
Different tools have been developed for the detailed simulation of critical components. For instance, a 1D model for the simulation of SOFC and SOEC has been developed, calibrated, and validated. A 1D model for the simulation of oxygen membranes has also been developed.

HiPowAR Power Generation System

The European project HiPowAR is aimed at developing a novel concept for power generation based on oxy-combustion of NH_3. Differently from other oxy-fuel cycles, where oxygen production accounts for about 10 percentage points of efficiency loss and requires an expensive Air Separation Unit (ASU), oxygen production and pressurization and fuel combustion are integrated in a single membrane reactor component, with negligible energy consumption.
Several configurations with different complexity levels have been considered, and their performance has been estimated by means of 0D steady-state simulations. The maximum efficiency calculated is equal to 60.2%, assuming a maximum cycle temperature equal to 1350°C, sub-atmospheric expansion, and double reheating of the working fluid.
Although the HiPowAR project is not over and further simulations will provide more accurate and conclusive information, the efficiency of the HiPowAR system is expected to be comparable to that of a combined cycle, under optimistic assumptions. Considering the maturity and low cost of combined cycles, further benefits are required to support the feasibility of the HiPowAR concept. For instance, water and nitrogen are produced as part of the HiPowAR process, which is interesting considering that the intricate water-food-energy nexus must be carefully balanced in the future. Moreover, low NO_x emissions are expected from the HiPowAR process.
A 1D oxygen membrane model has been developed, which is deemed to be a useful tool for the prediction of temperature profiles inside the membrane reactor. The preliminary results obtained are sound and in line with expectations, and they allowed to get useful insights on the behavior of the reactor.
Finally, the use of hydrogen as fuel in the HiPowAR system could also be interesting, as benefits from the point of view of the cycle simplicity and efficiency are expected.
Applying the oxy-fuel HiPowAR concept for carbon capture applications is also interesting, since competitive technologies are significantly less efficient compared to a modern combined cycle.

Hybrid SOFC-GT Power Cycle

Although innovative, the HiPowAR system can be classified as a heat-to-work process where the Carnot efficiency limits the performance of the system. In order to overcome this limit, this thesis investigates, by means of steady-state thermodynamic simulations, different configurations of a hybrid power generation system integrating an SOFC with a Gas Turbine (GT), using ammonia as fuel.
The mild system pressurization required allows for evaporation of ammonia at low temperature (e.g., -15°C), which in turn provides a chilling effect as part of the process. For this reason, this system might be particularly suitable for applications where cooling is required, like powering data centers. Alternatively, ammonia evaporation can partly be integrated within the power system by cooling down the air at compressor inlet, decreasing its consumption. Adopting this approach, the hybrid cycle achieves a very large electric efficiency, equal to 79.6%.
Given the large potential of ammonia SOFCs, either as stand-alone systems or within highly efficient hybrid cycles, more detailed experimental and numerical investigations are required. As part of the PhD activities, an experimental test rig has been set up at University of California, Irvine (USA), with the final aim of testing SOFCs using ammonia as fuel. However, due to hurdles partly related to the use of a corrosive and toxic fuel, it was not possible to run experiments.
On the other hand, the 1D SOFC model developed in this thesis can be expanded relatively easily by also considering operation with ammonia, allowing the estimation of the active area required and a more comprehensive comparison between hybrid configurations and SOFC operating conditions. Therefore, this activity is suggested as a possible future development of this work.

Production of Green Ammonia

In order for ammonia to be considered a clean fuel, it must be produced using renewable primary energy, like biogenic methane or hydrogen produced by renewable electricity in electrolysis. This thesis investigates several configurations for a particular type of green ammonia production plant, where hydrogen is produced using SOEC technology, and nitrogen is produced without using a dedicated ASU.
Starting from a concept found in the literature, innovative configurations have been proposed, significantly improving the overall plant efficiency. The 1D solid oxide cell model developed in this work has been used to gain relevant insights, especially on the size of the SOEC component.
The average current density estimated using the 1D SOEC model is low in all configurations. To address this issue, it is suggested to operate the SOEC at higher voltage (e.g., thermoneutral), atmospheric pressure, and avoiding pure oxygen at the air electrode. Aside from decreasing the investment costs, these measures would also simplify the system design by eliminating the complications related to high-pressure operation, and by reducing thermal stresses and degradation issues within the SOEC component.

EXPERIMENTAL WETTABILITY ANALYSES AND COMPUTATIONAL FLUID DYNAMICS MODELING OF INDIRECT EVAPORATIVE COOLING SYSTEMS

Roberta Caruana - Supervisor: Manfredo Gherardo Guilizzoni

1. Introduction, motivation, and objectives of the work

Nowadays, heating, ventilation, and air conditioning (HVAC) systems play a crucial role in buildings, because of the need for adequate comfort conditions, the growth of population, and the increasing global average temperatures due to climate change. In this context, Indirect Evaporative Cooling (IEC) and Dew-Point Indirect Evaporative Cooling (DIEC) systems have gained popularity, as they use the latent heat of vaporization of water to cool down an air stream, without increasing its humidity ratio. In fact, water is sprayed into the working (secondary) air channels with the aim of forming a film on the heat exchanger plates, while the product (primary) air is cooled maintaining a constant humidity ratio. Therefore, these systems provide optimal thermohygrometric conditions, with a much lower energy consumption compared to traditional HVAC systems based on the vapor compression cycle. For these reasons, the necessity of accurate models to predict their behavior and performance has recently arisen. Nevertheless, existing analytical and numerical models for IEC and DIEC systems either assume fully wetted heat exchanger plates, thus leading to a loss of accuracy under certain conditions, or the wettability of the plates is estimated through data-driven approaches, which may reduce the model generality. Consequently, the primary objective of this work was to develop an experimentally validated Computational Fluid Dynamics (CFD) model that integrates experimental wettability data as input parameters, to ensure a more accurate prediction of IEC systems performance. Additionally, as a secondary aim of this work, the feasibility of employing innovative foamed materials for DIEC systems applications was experimentally investigated, in collaboration with the University of Córdoba and the Andaltec company.

2. CFD model for IEC systems: development, validation, and results

To develop the final CFD model for IEC systems operating under wet conditions, which was implemented using the open-source software OpenFOAM, three main steps were necessary. The first step involved an extensive experimental analysis of the plates wettability, considering parameters such as the static and dynamic contact angles, the spreading factor, and the reversible work of adhesion. These measurements were conducted on three commercial heat exchanger plates (an aluminum uncoated surface, AL, a standard epoxy coating, STD, and a hydrophilic lacquer, HPHI) in both clean and fouled conditions, namely when limescale deposits altered surface properties. The results of this analysis were used as input parameters for the final CFD model.

The second step was the development of a CFD model for IEC heat exchangers operating under dry conditions, which was used as a fundamental step toward the development of the final model. This preliminary model was validated by comparison with existing experimental data for a cross-flow IEC heat exchanger. The validation results showed that the average and maximum discrepancies between numerical and experimental data were 1.7% and 4.9% for the secondary air outlet temperature, 4.0% and 5.3% for the primary air outlet temperature, 6.0% and 8.1% for the dry-bulb effectiveness, respectively. After validation, the model was employed to analyze the influence of the plate geometry on the IEC system performance.

The third and final step was the development of the final CFD model for IEC heat exchangers operating under wet conditions. This model was designed to take into account the real plates wettability and incorporated a lumped parameter approach for film evaporation modeling. The validation was performed again by comparison with existing experimental data for three cross-flow IEC heat exchangers, using the AL, STD, and HPHI plates. The validation results showed that the average and maximum errors were 3.2% and 6.2% for the primary air outlet temperature, 3.7% and 6.7% for the secondary air outlet humidity ratio, 4.0% and 7.3% for the wet-bulb effectiveness, respectively. After validation, the last step of this analysis was the assessment of the differences in the performance of IEC heat exchangers using the three commercial plates previously analyzed, both in clean and fouled conditions. From this analysis it emerged that the numerical results were consistent with the experimental wettability results previously obtained, as an improvement in the wettability of the plates leads to a significant improvement in the system performance. However, in the design of IEC heat exchangers, it is important to consider not only the wettability of the clean surfaces, but also how it changes when the plates are covered with limescale deposits, in order to ensure the long-term reliability of the system.

3. Experimental analyses on foamed materials for DIEC system

In this experimental study, the feasibility of using new porous materials fabricated through additive manufacturing (AM) techniques as coatings for DIEC systems plates was investigated. In particular, two foamed materials indicated as white foam (DW) and black foam (DB) were tested, using ten different samples per material (D1-D10). These analyses were aimed at assessing the water absorption, capillarity, porosity, and wettability of the samples. The results indicated that the DW material shows better performance parameters than the DB material in all the performed tests. Additionally, the D1 configuration emerges as the most promising for both materials. However, although the results were less favorable when using DB material compared to DW, in both cases the criteria necessary to produce an effective DIEC systems were met. Consequently, these results highlighted the suitability of foamed materials manufactured using AM techniques in DIEC systems applications.

4. Conclusions and possible future developments

In this work, a numerical CFD model for the prediction of the behavior and performance of IEC heat exchangers operating under wet conditions was developed. The model, based on experimental wettability results and on its simplified version for heat exchangers operating under dry conditions, was successfully validated by comparing the numerical results with existing experimental data. After validation, the model was used to assess the influence of the plate wettability on the IEC heat exchanger performance. Additionally, an analysis of the feasibility of using foamed materials produced through AM techniques as wetting materials in DIEC systems was carried out, in collaboration with the University of Córdoba and the Andaltec company. From this analysis, it emerged that the criteria necessary to produce an effective DIEC system were met for both the studied materials, but that identified as DW showed the most promising results. Finally, some interesting aspects that could be investigated as future developments of the work are:

- A more in-depth analysis of the effect of the geometry of the plates on the IEC heat exchanger performance, both in dry and wet conditions.
- An extensive analysis of the effect of using plates characterized by different wettability on the performance of IEC heat exchangers.
- The fabrication of DIEC systems using the analyzed foam materials in order to evaluate their performance under real operating conditions.

DEVELOPMENT OF AN X-RAY IRRADIATION FACILITY FOR NON-DESTRUCTIVE TESTING

Francesco Casamichiela - Supervisor: Andrea Pola

This PhD thesis presents the design, development, and characterization of *RETINA*, a custom-built X-ray Computed Tomography (XCT) facility developed for non-destructive testing (NDT) of electrochemical devices. The project was carried out within the *Energy for Motion* initiative, with the goal of establishing an imaging platform capable of 3D scans of medium-sized samples (up to ~15 cm) for morphological and structural analysis. The facility was designed and built from scratch, integrating an X-ray tube, a sample positioning system, and a detector, all controlled via a dedicated LabVIEW-based software, developed during the PhD. The system achieves a spatial resolution of approximately 90 µm, enabling investigations of internal features in energy storage devices such as batteries and fuel cells at the device level.

The thesis starts by detailing the technical choices behind the design of RETINA, discussing the constraints and trade-offs involved in selecting the system components. The constraints were dictated by the only item that was initially available: the X-ray source. The source is an RTC1000-HS high-intensity medical X-ray tube from IAE, chosen for its high-flux output, which is significantly higher than that of microfocus sources commonly used in lab-based XCT. This enables faster imaging but comes at the expense of spatial resolution, requiring a careful balance between exposure time, contrast, and image sharpness. The positioning system consists of three translational and one rotational, high-precision stages based on stepper motors, made by THORLABS. The facility is equipped with imaging detectors in indirect lens-coupled configuration, where X-rays are converted into visible light by a scintillator before being captured by a CCD/CMOS camera. This setup allows for flexible adjustments in field of view and magnification. A detector with a resolution of about 90 µm resolution was bought from Neutronoptics. A second detector was designed to have a high-sensitivity and a 50 µm resolution and was assembled during the PhD work.

A fundamental part of this work was the characterization of both the X-ray source and the detector, which was carried out through a combination of experimental measurements and numerical modeling. The X-ray tube spectrum was calculated using the Monte Carlo code FLUKA, implementing a detailed representation of the anode geometry and material composition. The fluence spectra per unit electron were scored for different values of the kVp and different angles. This allowed to have a model of the emission spectrum of the tube for any current and distance from the focal spot. The source X-ray spectra were then measured using a collimated HPGe detector to validate the simulations.

A 1 mm-diameter pinhole and a specific configuration were employed to minimize the detector dead-time. Measurements were performed both without added filtration and with Al and Cu filters. The measured spectra were unfolded with a Bayesian approach to correct for spectrometer response (calculated via the FLUKA code). A comparison of the simulated and measured spectra allowed to determine the inherent-filtration, showing excellent agreement with the Monte Carlo predictions both for filtered and unfiltered spectra. Figure 1 displays the comparison for 100 kVp without added filtration (a) and for 80 kVp with an added filtration of 0.6 mm Cu.

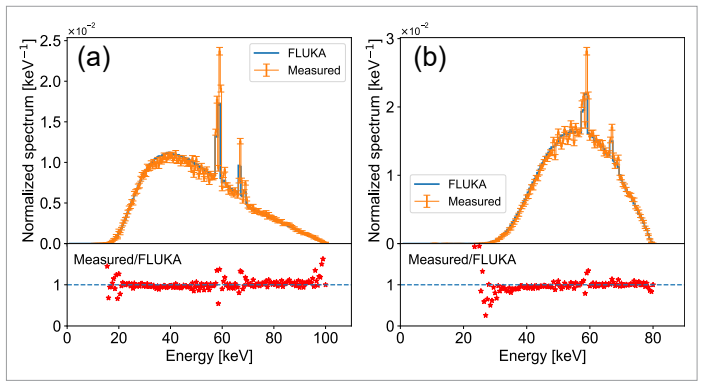

Fig. 1 - Example of the fitting of the numerical spectra (FLUKA) to the measured ones for the calculation of the inherent filtration: (a) 100 kVp; (b) 80 kVp + 0.6 mm Cu filtration. Error bars are only reported in the measured spectra for clarity. The ratio between the measured and numerical spectra is reported below each figure, showing the good agreement between the data.

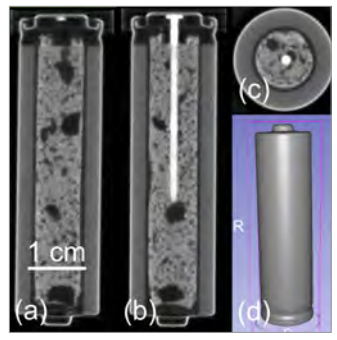

Fig. 2 - X-ray Computed Tomography (XCT) of a commercial 1.5 V battery performed at the RETINA facility: (a) and (b) vertical slice, (c) horizontal slice, (d) 3D rendering of the reconstructed volume. Data are displayed with the 3D Slicer software.

The X-ray detectors underwent an extensive characterization process, focusing on spatial resolution, contrast, and signal response. The Modulation Transfer Function (MTF) of the detectors was determined using the sharp-edge method, and the obtained resolution was compared with the one measured using resolution test patterns, obtaining a good agreement. Moreover, a theoretical model was developed to describe the degradation in resolution caused by re-absorption of characteristic X-rays and by the light scattering within the scintillator. Unlike existing models, this work introduced a simplified expression for the MTF of re-absorbed K-shell X-rays. The theoretical model was applied to the detectors by fitting experimental data of MTF, leading to a precise estimation of the scintillator's light-transport parameters. This allows to calculate the detector response function.

Building upon the source and detector characterization, an XCT simulation tool based on the ray-tracing engine of FLUKA was developed, which can be used to optimize imaging configurations of samples. This simulation framework models the entire imaging chain, incorporating source properties, sample attenuation, and detector response. One key application of the simulation was to determine the optimal scanning conditions for a specific sample geometry. The model was validated by comparing simulated and experimental radiographic images, confirming its predictive accuracy. This approach enables systematic optimization of imaging protocols for different types of samples, reducing trial-and-error in experimental setups.

To evaluate the facility capabilities, radiographic and tomographic scans were performed on two electrochemical devices: an aged Pb-acid battery electrode and a fully discharged commercial alkaline battery. In the first sample, RETINA was able to provide sufficient transmission and resolution to detect cracks of about 200-400 µm in the spine of the aged electrode. A segmentation of the grid provides a map of these crack, which can be used to understand the degradation phenomena of the battery. An XCT was performed on a commercial 1.5 V alkaline battery after complete discharge. The tomography reveals sub-mm porosities in the Zn-anode. Slices of the XCT, as well as a 3D rendering are shown in Figure 2.

Beyond its applications in electrochemical research, RETINA has the potential to be adapted for a wide range of non-destructive testing tasks. Possible future developments include the integration of complementary techniques, such as X-ray fluorescence (XRF) for chemical composition analysis or dual-energy imaging for improved material differentiation. These enhancements could expand the range of materials and structures that can be investigated, making RETINA a more versatile tool for advanced imaging studies.

OPTIMIZING GRAPHITE-MODERATED REACTORS DECOMMISSIONING AND WASTE MANAGEMENT: A MULTIDISCIPLINARY APPROACH

Riccardo Chebac - Supervisor: Alessandro Antonio Porta

The decommissioning of graphite-moderated reactors presents unique challenges compared to other nuclear facilities due to the large volume of radioactive waste, long-lived radionuclides, and the management of Wigner energy. While over 700 reactors of various types have been decommissioned worldwide, graphite-moderated reactors remain a distinct category requiring specialized strategies. This thesis explores optimization methods across three key decommissioning phases: characterization, dismantling, and waste management. Graphite has played a critical role in nuclear technology as a moderator and reflector, with continued relevance in future Gen IV reactors. However, its decommissioning is more complex than that of PWRs and BWRs due to the handling of large reactor cores and radioactive graphite containment. This thesis contributes to ongoing research by refining mechanical characterization techniques, developing an innovative graphite handling system, and exploring electrochemical decontamination in molten fluoride salts.

Mechanical Characterization of Nuclear-Grade Graphite

The characterization phase is crucial in decommissioning graphite-moderated reactors, ensuring accurate assessment of irradiated graphite's mechanical properties. This research introduces an innovative sampling approach that replicates in-reactor graphite geometry, enhancing the reliability of material behaviour analysis. Experimental tests measure the flexural and compressive strength of non-irradiated graphite, along with its Young's modulus. These results feed into an FEM model, improving prediction accuracy by over 30% compared to traditional methods. A key breakthrough is the correlation between Vickers microhardness and graphite's mechanical properties, enabling in-situ characterization. This approach eliminates the complexities of conventional mechanical testing, streamlining assessment and improving the safety and efficiency of decommissioning operations.

Remote Graphite Handling Device Development and Testing

Graphite removal presents a unique set of challenges, primarily due to the radioactive nature and structural and mechanical complexity of irradiated graphite. The objective of this phase is to develop and implement an advanced system for safely and efficiently handle and remove graphite blocks during decommissioning. The primary challenges include ensuring operational safety, minimizing radiation exposure to workers, and optimizing the efficiency of the dismantling process. In response to these challenges, the research focuses on the development of an advanced graphite grabbing system. This system is designed to enhance the retrieval of graphite blocks by improving grip strength, reducing slippage, and incorporating safety features to prevent accidental release. Following the design validation, a prototype of the graphite grabbing system is constructed and subjected to a series of tests to evaluate its performance. These tests simulate the conditions encountered during actual dismantling operations. The results demonstrate a safety factor exceeding 3, indicating a robust design capable of safely handling the anticipated loads with a significant margin of error and beating industrial competition. The system showcases a four-fold increase in lifting capability compared to industrial vacuum systems. Additionally, the system's design minimizes the potential for graphite block damage during handling, reducing the risk for crack propagation and generation of graphite dust and associated radiation exposure risks.

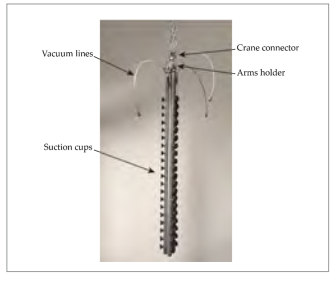

Fig. 1 - First mock-up for full-scale testing

Electrochemical Decontamination of Silver from Nuclear Graphite in Molten FLiNaK at 700°C

The decommissioning of graphite-moderated nuclear reactors presents a significant challenge, particularly in managing graphite waste, which is both voluminous and long-term radioactive. The sustainability and environmental stewardship of nuclear technologies necessitate innovative approaches to reduce the volume and radioactivity of such waste. Attractive solutions have been found such as in molten-salt oxidation and electrochemical treatments. This study investigates the electrochemical decontamination of silver from nuclear graphite using molten FLiNaK at 700°C, offering insights into a novel method that could mitigate disposal costs, volumes, and environmental impact. The study utilizes non-irradiated IG-110 nuclear-grade graphite, subjected to a process involving electroplating and subsequent deplating of silver in a molten FLiNaK salt environment. The choice of FLiNaK, composed of lithium fluoride, sodium fluoride, and potassium fluoride, offers a high electrochemical window that facilitates the removal of electropositive metals like silver. The electroplating phase successfully deposits silver onto the graphite surface, creating a model system for studying decontamination. SEM/EDS analyses confirm the deposition of elemental silver and provide detailed insights into the morphology and distribution of the plated silver particles. The subsequent deplating phase demonstrates the effective removal of silver from the graphite, underscoring the electrochemical process's efficiency in reducing surface contamination.

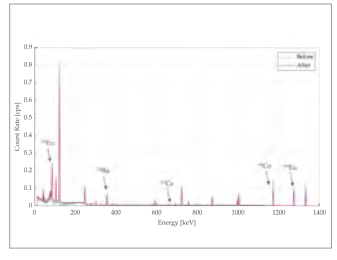

Fig. 2 - Gamma spectra before and after the electrochemical decontamination

Irradiated A3 Graphite Matrix Decontamination in Molten FLiBe at 600°C

Building on the foundation established in the previous section, this study advances the exploration of fluoride electrochemical decontamination processes by examining the decontamination of an irradiated A3 graphite matrix in a molten FLiBe electrochemical bath at 600°C. The A3 graphite matrix, subjected to 2.69 DPA irradiation and utilized in TRISO fuel particles, presents a more realistic contamination scenario for testing. The preference for FLiBe, a primary coolant candidate in MSR and FHR designs, is informed by its historical application in the Molten Salt Reactor Experiment and its potential for in-situ decontamination applications. A four-electrode configuration is utilized, with irradiated A3 graphite as the working electrode and a platinum wire serving as the counter electrode. A silver rod and a tungsten wire act as the quasi-reference electrode and dynamic reference electrode, respectively. The methodology aims to evaluate the effectiveness of FLiBe in removing gamma emitters and selectively separating ^{14}C, based on its propensity for being found in the near-subsurface layer of graphite and its binding energy with graphite, which could facilitate its removal in high-temperature, weakly oxidizing conditions.

The experimental outcomes demonstrate an increase in current densities by a factor of 12 compared to previous studies, suggesting enhanced decontamination rates. However, the selective separation of $^{14}CO_2$ was not conclusively observed. Gamma spectra analysis post-decontamination indicates a reduction in specific activities for several radionuclides, with an overall reduction in the graphite sample's specific activity of approximately 10% within one hour.

Conclusion and Future Developments

The comprehensive approach taken in this thesis to tackle the decommissioning of graphite-moderated reactors sets a foundational framework for future advancements. The integration of insights from mechanical characterization, innovative extraction systems, and electrochemical decontamination forms a cohesive strategy that promises to enhance the decommissioning process significantly. As the field moves forward, it is imperative to continue the synergy between these research areas, focusing on refining methodologies and technologies to meet the unique challenges posed by graphite-moderated reactors. The collective research efforts presented lay the groundwork for a more efficient, safe, and informed approach to decommissioning, marking a significant step towards the sustainable management of nuclear legacy waste.

SYNTHESIS AND IN-SITU CHARACTERIZATION OF 2D MATERIALS ON METALS

Paolo D'Agosta - Supervisors: Carlo Spartaco Casari, Andrea Li Bassi

The drive for miniaturization and enhanced functionality in electronic and optoelectronic devices has propelled two-dimensional (2D) materials to the forefront of materials science. Characterized by their atomic-scale thickness with extremely high surface-to-volume ratio, they exhibit fascinating properties that diverge significantly from their bulk counterparts. The fundamental principle governing these unique characteristics is quantum confinement, which restricts the movement of electrons within the material, leading to dramatic alterations in their electronic band structures and optical responses. The ability to precisely tune the electronic properties of 2D materials through various means, such as doping, strain engineering, and the creation of heterostructures, opens up various possibilities to tailor their functionalities to specific applications, in fields such as optoelectronics, catalysis, energy storage and conversion, and sensing. Furthermore, their exceptional mechanical strength makes them ideal candidates for flexible and transparent electronic devices. Among the vast family of 2D materials, layered chalcogenides and carbon-based networks have garnered significant attention among researchers. Transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), exhibit a remarkable transition from an indirect to a direct bandgap as their thickness is reduced to a single layer, making them highly attractive for optoelectronic applications. Bismuth telluride (Bi_2Te_3) is instead a layered topological insulator with unique electronic and thermoelectric properties. Finally, carbon-based 2D materials like graphene and graphdiyne offer exceptional electrical conductivity and mechanical strength. Graphdiynes-like (GDY) structures, with their unique networks combining *sp*- and sp^2-hybridized carbon atoms, exhibit tunable bandgaps ranging from semimetal to semiconducting. The synthesis of high-quality 2D materials with precise control over their thickness, structure, and properties remains a significant challenge. Traditional fabrication methods often suffer from limitations in scalability and time efficiency. To address these challenges, bottom-up and solvent-free synthesis strategies, such as on-surface synthesis (OSS) and pulsed laser deposition (PLD), have emerged as promising alternatives. These methods, performed under ultra-high vacuum (UHV) conditions, enable precise control over the growth process, ensure high interface purity, and allow for in-situ characterization of the resulting materials. I employed scanning tunneling microscopy and spectroscopy (STM/STS), low-energy electron diffraction (LEED), Raman spectroscopy, and angle-resolved photoelectron spectroscopy (ARPES), which play a crucial role in understanding the atomic structure, electronic properties, and vibrational features of 2D materials. STM provides atomically-resolved images of the material surface and monitors its morphology and growth, while LEED reveals the symmetry of the atomic lattice. Raman spectroscopy probes the vibrational modes of the material, giving insights into its crystal structure and bonding geometry; finally, STS and ARPES measure the local and global electronic band structure of the material. The choice of metal surfaces as supporting substrates is also critical, as they not only enable the use of powerful techniques like STM/STS or ARPES, but also influence the growth process and electronic properties. Therefore, understanding the 2D material-metal interface is essential for designing and optimizing electronic devices.

My PhD thesis explores the fundamental properties of semiconducting 2D materials grown on metal surfaces, focusing on their morphological, structural, electronic, and vibrational characteristics. The PLD technique is used to fabricate inorganic 2D materials, such as MoS_2, WS_2, and Bi_2Te_3 single layers, as well as MoS_2–WS_2 heterostructures. For the synthesis of carbon-based GDY-like nanostructures, molecular precursors like 1,3,5-tris(bromoethynyl)benzene and 1,4-bis(bromoethynyl) benzene are employed to initialize the OSS process, allowing for precise control over the geometry of the resulting network. A detailed characterization of the growth process and morphology of the fabricated 2D materials and heterostructures is carried out using STM and LEED; concurrently, Raman spectroscopy is employed to elucidate charge transfer and induced strain effects. These techniques are used synergistically not only to understand the influence of 2D material-substrate interactions and synthesis parameters, but also to monitor the structural evolution of GDY-like organometallic systems under thermal treatments and their transition towards all-carbon networks. Finally, a thorough analysis of the electronic band structure and orbital character of GDY-like organometallic frameworks is conducted by employing ARPES and STS to map electronic states and associate their features to real-space lattice characteristics.

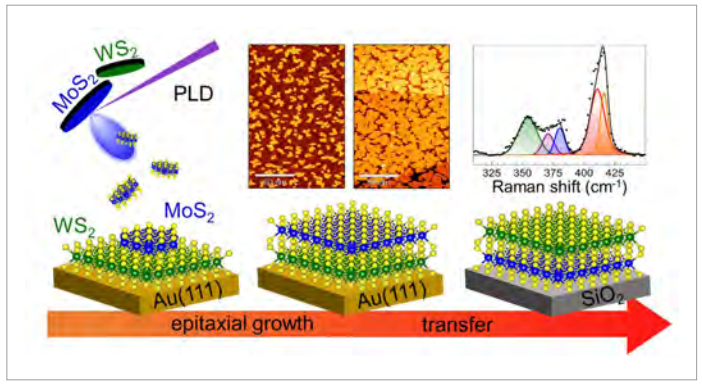

Fig. 1 - Schematic of the PLD synthesis of MoS2/WS2 heterostructures on Au(111) and their subsequent characterization by STM and Raman spectroscopy, aimed at monitoring the growth process and understanding substrate interactions.

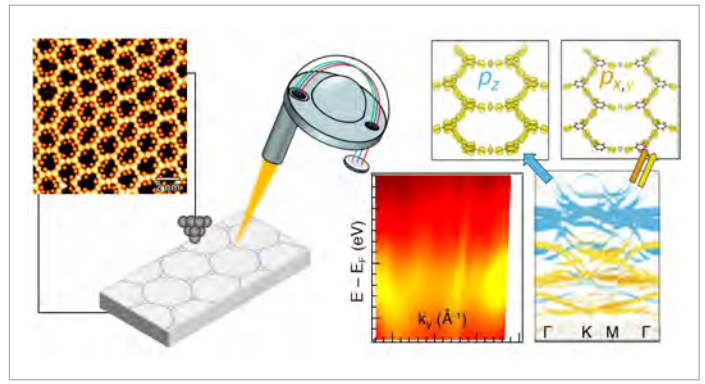

Fig. 2 - Schematic of the characterization process of OSS-produced GDY-like organometallic network on Ag(111) involving STM/STS and ARPES measurements, aimed at mapping the global and local electronic structure.

NUMERICAL INVESTIGATIONS OF LASER-DRIVEN PHOTON AND PARTICLE SOURCES WITH NANOSTRUCTURED MATERIALS AND THEIR APPLICATIONS

Marta Galbiati - Supervisor: Matteo Passoni

Tutor: Andrea Pola

Laser-driven sources of photons, ions, and positrons are an appealing and rapidly evolving field of research that leverages the interaction of high-intensity femtosecond laser pulses with specifically designed targets. During these interactions, it is possible to generate and accelerate particles to relativistic energies, leading to applications in fundamental physics studies, materials science and nuclear physics. The triggering mechanism behind these laser-driven sources is the acceleration of electrons, which in turn enables proton acceleration via Target Normal Sheath Acceleration (TNSA) in solid foils. In addition to proton acceleration, high-energy photons can be produced through two primary mechanisms. The first is bremsstrahlung radiation, which occurs especially when high-energy electrons pass through a dense, high-Z material, leading to the emission of photons. The second mechanism is Non-linear Inverse Compton Scattering (NICS), a synchrotron-like process where electrons emit because of their interaction with the strong laser field. These photons, in turn, can initiate pair production processes in plasma interactions. Specifically, two processes can play a role: Non-linear Breit-Wheeler (NBW) pair production, where a high-energy photon interacts with the strong laser field to produce an electron-positron pair, and Bethe-Heitler (BH) pair production, where a high-energy photon interacts with a nucleus to generate a pair.

A novel target concept, known as the Double-Layer Target (DLT), has emerged as a promising candidate to trigger and enhance all these processes simultaneously. A DLT consists of a low-density, nanostructured foam layer produced via pulsed laser deposition, which is placed on top of a solid substrate. This combination provides unique advantages in laser-plasma interactions, allowing for optimized absorption of laser energy, efficient electron acceleration to relativistic velocities through direct-laser acceleration, and enhanced TNSA. It also provides a solid and possible high-Z substrate, ensuring bremsstrahlung and BH pair production, as well as laser reflection, which favors collisions with electrons and photons necessary to boost NICS and NBW. However, despite its potential, the study and application of DLTs remain limited, necessitating further investigations into their properties and performance.

This thesis presents an extensive numerical investigation into laser-DLT interactions, employing advanced particle-in-cell (PIC) simulations coupled with Monte Carlo techniques. These simulations explore a wide range of laser intensities, spanning from 10^{18} up to 10^{22} W/cm^2, to analyze the effects of direct laser acceleration of electrons, self-focusing phenomena, and laser reflection within the DLT structure. The findings reveal that the characteristics of both layers within the DLT play a critical role in determining the efficiency of ion acceleration, photon emission, and pair production. Specifically, homogeneous, low-density, and long foam layers enhance high-energy particle acceleration and photon generation. Additionally, high-Z, high-mass-density solid substrates improve photon and positron production due to the increased reflectivity and atomic number dependence of bremsstrahlung and BH pair production.

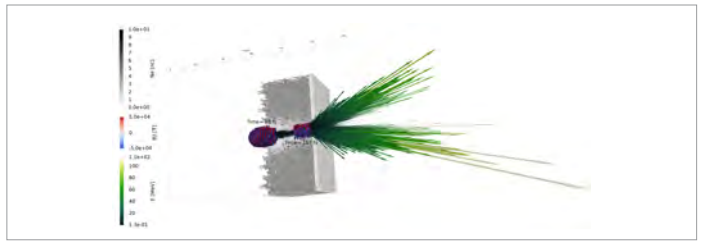

Fig. 1 - Snapshot from a 3D simulation of laser-DLT interaction at intensity 3.42×10^{21} W/cm^2 with nanostructured foam model. The laser pulse at two different times (98 fs and 157 fs from the start of the simulation) is depicted by the magnetic field component B_z at 50 kT. The target, cut at half of the simulation box, is represented by its electron density Ne at 157 fs. NICS photons are represented as arrows positioned where they are emitted, coloured based on energy E, and scaled and oriented according to their momentum components.

One of the core aspects explored in this study is the modeling of nanostructured plasmas due to the foam and their interactions with high-intensity lasers. The proposed modeling approach tries to mimic the experimentally observed foam structures. See the model applied to a PIC simulation in Figure 1. Simulations have demonstrated the importance of accurate nanostructure simulation since its presence can disrupt coherent electron acceleration, thereby slightly reducing ion acceleration and photon production at high energies.

The thesis also investigates ion acceleration mechanisms in compact laser systems, focusing on optimizing proton sources with 20 TW lasers. It has been shown that MeV-scale proton beams with laser-to-proton conversion efficiencies exceeding 2% can be achieved under specific conditions. Additionally, studies in sub-TW intensity regimes have highlighted the significant role of field ionization effects and nanostructure morphology in enhancing laser absorption, demonstrating that at lower intensities, the DLT approach can offer significant advantages.

Photon generation has been analyzed in detail through the study of both NICS and bremsstrahlung mechanisms. Their properties have been thoroughly examined, showing that NICS emissions follow a bilobate pattern (visible in Figure 1), while bremsstrahlung leads to more isotropic emission. The efficiency of these processes, which can reach a few percent in optimal configurations and energies of hundreds of MeV, depends on the choice of target parameters. Specifically, long, low-density foams enhance photon production, making DLTs an attractive option for photon sources.

The thesis also explores positron production through both NBW and BH processes, revealing that while the former remains a topic of great theoretical interest, it exhibits very low efficiency in practical applications. NBW is enhanced by appropriate choices of foam and substrate properties like in NICS emission: enhancing photon emission in long foams and laser reflection with dense and high-mass solid substrates at the highest possible laser intensity are the key steps for the observation of this process in DLTs.

While the DLT scheme may not be the optimal solution for achieving the highest energy outputs in individual particle acceleration or radiation generation processes, its strength lies in its versatility and adaptability. The ability to generate multiple types of particles in a single interaction makes it an attractive platform for various applications. To fully exploit its potential, future research should focus on refining laser pulse modeling in simulations, improving diagnostic techniques, and conducting dedicated experimental campaigns. Preliminary results from recent experimental efforts at facilities such as VEGA3 (Spain) and Apollon (France) have highlighted both the advantages and challenges associated with DLTs, including the need for meticulous handling in high-repetition-rate experiments.

In conclusion, this thesis contributes to the ongoing efforts in laser-plasma interaction research by providing a comprehensive numerical investigation into the capabilities of DLTs. The results obtained emphasize the importance of target design in optimizing laser-driven particle sources and point out the need for further theoretical and experimental work to refine and validate these findings. With continued advancements in laser technology and computational modeling, DLT-based particle sources could play a crucial role in fundamental physics and applications in imaging, materials and nuclear science.

NUMERICAL APPROACHES FOR THE OPTIMIZATION OF GAS TRANSPORTATION NETWORKS

Lavinia Marina Paola Ghilardi - Supervisor: Emanuele Martelli

Co-Supervisor: Francesco Casella

This thesis provides comprehensive mathematical approaches to optimize gas pipelines operation and apply the methodology to real-world transportation pipelines. The objective is to support decisionmaking of gas Transmission System Operators (TSOs) to minimize the CO2-eq emissions related to gas compression work. The optimization algorithms model the process with high level of detail in a unified framework, considering the gas transport dynamics, compressors and control valve operation. The methodology is validated with real data, and it is applied to the Italian network, showcasing the potential of the optimization to improve environmental sustainability. Gas networks are complex systems which convey natural gas from import nodes, extraction sites, and regasification facilities to delivery points. These large-scale systems consist of pipelines, control valves and compressor stations, which maintain an adequate pressure level. In these stations, the compressors are mechanically driven by gas turbines, which consume a small portion of the transported natural gas to drive the compressors. Over the total transported gas, approximately 1-4% is used to fuel gas compressor stations. The companies responsible for managing natural gas transmission networks are the gas TSOs. Unlike electrical grids, where incoming and outgoing power must be balanced instantaneously, gas transmission networks are characterized by a variation of the linepack over the day. The linepack plays a crucial role in managing the gas flow and ensuring the operational flexibility of the network. Therefore, accounting for these dynamics is crucial to properly manage the gas grid. Nevertheless, commercial tools used by gas TSOs rely on steady-state models. Similarly, in academic literature, algorithms capable of handling complex switching decisions (both mixed-integer and nonlinear models) typically adopt a steady-state assumption. Most studies use an idealized model of natural gas compressors and lack validation with real data. Dynamic models are generally applied to small to medium-sized networks with fewer than a hundred nodes. This research aims to improve the accuracy of gas network modelling, while maintaining the interface with industrial datasets and applying the algorithms to real-world problems. The optimization problem for gas network operation is formulated as a nonconvex Mixed Integer Nonlinear Program (MINLP). Gas transport in pipelines is governed by nonlinear dynamic Euler conservation equations, while control valves are controlled to comply with pressure limits. Compressor stations comprise a set of centrifugal compressors and their drivers, each characterized by performance maps and limits. These stations operate in various discrete configurations of machines and bypass/check valves. Solving this nonconvex MINLP for real large scale networks, comprising thousands of elements, can be challenging. Therefore, we develop a solution strategy combining graph-preprocessing (model reduction), Mixed Integer Linear Programming (MILP) and Nonlinear Programming (NLP) algorithms. Graph preprocessing procedures allow to directly apply the algorithm to real data, systematically reducing the number of elements of the graph from thousands to hundreds. The MILP algorithm, which requires longer computational times, determines the scheduling of compressors, representing integer variables that change less frequently (e.g., every 4-6 hours). The nonlinear algorithm provides the accurate optimal operation and updates the solution in real-time control, while also handling frequent switching conditions, such as flow reversal and valve control. By combining these two methods, we leverage the good starting point provided by the MILP and the fast local solution capabilities of the NLP. The Mixed Integer Linear Program is derived by linearizing the gas conservation equations in the pipes and the performance maps of the compressors. To solve the full-scale Italian gas pipelines, the problem is further decomposed. Due to its strategic location, this network can operate with numerous combinations of compressor scheduling and flow reversals. Hence, we develop a heuristic two-stage decomposition based on solving two MILP problems. Given the scheduling decisions, the Nonlinear Programming (NLP) algorithm optimizes the compressors loads and network operation. Complementarity conditions and smoothing techniques are applied to model control valves and flow reversals. The NLP improves the accuracy of the MILP, and it can be solved to local optimality in fast computation times by NLP solvers. This enables the algorithm to be used in the economic-oriented Nonlinear Model Predictive Controller (eNMPC), frequently updating the solution. We propose a formulation based on stabilizing and cyclic steadystate constraints. While the eNMPC is applied for gas pipelines operation, the methodology can find a wider application on any periodic process, guaranteeing asymptotic stability properties without the tuning of regularization parameters. The methodology is validated against real data, demonstrating the capability of the model to capture network dynamics with limited deviations from data. Subsequently, the algorithms are applied to a test network, comparing the nonlinear smoothed formulation with the MILP approximation. The NLP increases the accuracy of the solution and handles control valves and flow reversals in reduced computational time. This allows its application in the eNMPC, which effectively controls the system in cyclic operation. Following these foundational steps, we apply the methodology to the Italian gas network. The algorithms support day-ahead decision-making, where gas operators plan compressor scheduling and loads for the next day provided the initial state of the network. Additionally, algorithms are used to compare current strategies with the optimal cyclic steady state. The outcomes emphasize the key role played by the spatial pressure distribution of the gas across the network. The optimization of these variables, along with the compressors operating point allows to reduce the ideal work delivered to the fluid and to run compressors more efficiently. This combined effect allows to reduce the CO2-eq emissions of the compression process. The benefits are particularly significant when gas operators have less experience with the import-export regime. We also examine the introduction of electrocompressors in the pipelines, which exhibit increased efficiency and operational flexibility with respect to the gas turbine counterpart. Additionally, they can leverage periods of low electricity carbon intensity, significantly improving the sustainability of the process in presence of high renewable production.

Fig.1 - Italian gas network [adapted from www.snam.it]

MULTISPECTRAL IMAGING AND CORRELATION OF IMAGE SIGNATURES OF PV FAILURES WITH ELECTRICAL SIGNATURES

Lukas Koester - Supervisors: Giampaolo Manzolini, David Moser

Photovoltaic (PV) energy systems have become a key driver in the transition towards renewable energy sources. Ensuring their reliability and best possible performance is crucial for economically beneficial and safe energy supply, which makes optimal operation and maintenance practices necessary. This thesis contributes to that goal by improving PV module inspections in terms of economic defect analysis and developing advanced methods for luminescence-based inspection techniques.

A foundational step in this work was the development of the defect-characterization matrix, a tool that combines information on common PV module defects, performance parameters, and inspection techniques. This matrix enables quick insights and evaluations, supporting the identification and understanding of PV module defects and their expected severity. Beyond that, it allows to rate the effectiveness of various inspection methods identifying a large number of defects, showing the advantage of luminescence inspections. This superiority in detecting defects can be seen by comparing an electroluminescence (EL) image to visual and infrared thermography (IRT) images, as shown in Figure 1.

Building upon the comprehensive overview provided by the defect-characterization matrix, this thesis explores the economic impacts of individual defect occurrences in depth. By adapting the cost priority number methodology to single defect scenarios, potential costs of individual defect events can be calculated, and repair costs can be balanced against the missing income due to reduced performance. By application of this method in a case study, the variability of defect severity from an economic point of view is shown. This is an important step towards targeted interventions, predictive and prioritized maintenance, based on economic assessments, offering a foundation for real-world applications and decision support in PV plant maintenance strategies.

The advantages of luminescence inspection techniques in terms of defect detection efficacy are in contradiction to the higher costs to perform EL or daylight photoluminescence (DPL) inspections. To allow these techniques to compete with the common inspection technique IRT in price, the costs to conduct them have to be reduced by increasing the imaging speed. For this purpose, the EL-ready inverter was developed, which overcomes the time-consuming process of connecting external power supplies in the field. This development is expected to achieve doubling of imaging speed from reported 750 kWp/h towards 1,500 kWp/h, along with immense cost reductions for large-scale EL inspections. The development of a DPL-ready inverter allows for seamless operating point switching in the whole PV plant, a key step towards standardized DPL imaging in large-scale PV plants. The additional development of an automated operating point detection algorithm supports the application of DPL from unmanned aerial vehicles without synchronization between inverters and camera. These developments combined result in an estimated imaging speed of at least 1,200 kWp/h.

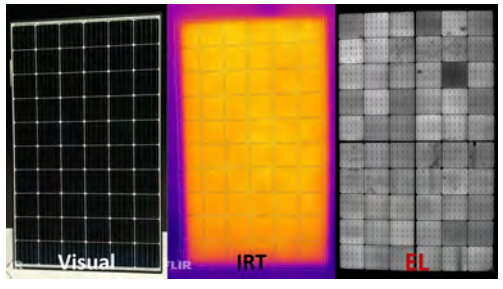

Fig.1 - Visual, infrared thermography (IRT) and electroluminescence (EL) image of the same module. While the first two don't show any deviation from normal status, EL reveals several defects, like (heavy) cracked cells, electrical mismatches, material impurities, and insufficient soldering.

Further investigations into the signal behaviors of EL and DPL have been conducted, particularly examining the effects of module heating during the current injection process of EL inspection. The effects of heating on PV module voltage, the consequences for the power supply unit, and the luminescence signal intensity are analyzed. Another inspection analyses the feasibility of quantifying DPL signals to estimate PV module performance and degradation by utilizing the exponential dependence of the luminescence signal to the cell voltage. The graph in Figure 2 shows how this method can reduce uncertainty of measuring open-circuit voltage, in comparison to a measurement by a portable IV tracer. These studies provide insights into the operational challenges and potential applications of the DPL technique, including temperature-, irradiance-, and geometry induced effects on signal intensity and their correction. The possibility of using DPL for performance assessment by signal intensity comparison is shown.

The advancements in PV module inspection techniques introduced in this thesis represent a significant step towards improving the predictive maintenance of PV plants. By providing tools for better defect identification and understanding, alongside innovative solutions for speeding up inspection processes, this work contributes to the ongoing effort to enhance the reliability, performance, and economic viability of PV energy systems. The integration of these methodologies into actual operation and maintenance practices, supported by intelligent automated flight planning and the adoption of digital twin concepts, promises to further optimize PV plant operation and maintenance in the renewable energy landscape.

In conclusion, this thesis contributes to the broader effort of strengthening PV system reliability and performance through improved operation and maintenance strategies with focus on PV module degradation and inspection. By offering novel insights and tools for defect identification, economic impact assessment, and enhanced inspection techniques, it paves the way for large-scale luminescence inspections and therefore to more informed and efficient maintenance practices.

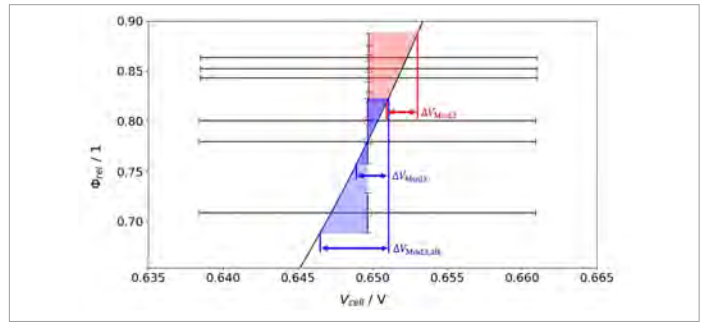

Fig.2 - Uncertainty of voltage measurement of a solar cell within a PV module: Measured with portable IV tracer (black horizontal error bars) vs. measured using the difference in photoluminescence signal intensity, Φ_{rel} (colored horizontal arrows).

NANOENGINEERED THIN FILMS FOR ELECTROCHEMICAL ENERGY STORAGE: FROM MATERIALS DEVELOPMENT TO FUNCTIONAL PROPERTIES

Andrea Macrelli - Supervisor: Andrea Li Bassi

Co-Supervisor: Carlo Spartaco Casari - Tutor: Valeria Russo

Nanostructured thin films with precisely controlled and tuneable nanoscale properties serve as ideal platforms for both fundamental materials science research and real-life applications, particularly in energy storage technologies. Indeed, an optimized nanoengineered film (thickness ~0.1–10 μm) enables the use of advanced materials that are impractical in bulk form while offering significant advantages for battery research and development. These benefits include simplified and innovative fabrication methods, increased surface area, self-supported structures, shorter diffusion paths for both electrons and ions, volume change accommodation owing to nanoporosity, and clean interfaces. In the present PhD thesis, an extensive experimental survey of the synthesis–structure–properties relationship of attractive materials for two classes of next generation batteries is reported. Specifically, manganese-based oxides (MnO_x and $Zn_xMn_{3-x}O_4$) are addressed as cathode candidates for aqueous Zn-ion batteries (AZIBs), in which the exploitation of divalent Zn^{2+} charge carriers and the use of a Zn metal anode coupled with a water-based electrolyte simplify the manufacturing process, increase the battery safety, and reduce the cost. In parallel, nanoporous silicon-based anodes are appealing for solid-state lithium-ion batteries (ASSBs), as replacing the liquid electrolyte with a solid ionic conductor leads to more compact and safer batteries by minimizing the risk of electrical short circuits and eliminating the hazards associated with traditional liquid organic electrolytes.

For both Mn-based oxides and Si, a careful nanoscale design is recommended to tackle the complex phase evolution of MnO_x in aqueous electrolyte and the massive volume expansion of Si upon lithiation. Herein, the primary objective was the attainment of a precise control over the nanomorphology, structure, phase, chemical composition, and finally functional properties of nanoengineered thin-film battery electrodes through an approach combining the versatility of pulsed laser deposition (PLD) with post-deposition thermal treatments in controlled ambient. By means of a multi-technique microscopic, spectroscopic, diffraction, and electrochemical characterization, a comprehensive investigation into the materials properties was carried out, in relation to both the synthesis conditions and the electrochemical behaviour, and specific materials-related open issues were sorted out. Briefly, the combination of O_2 deposition pressure and annealing temperature/atmosphere enabled the independent control of MnO_x phase and nanostructure (see Figure 1), and the stabilization of different phases (e.g., manganosite MnO, hausmannite Mn_3O_4, bixbyite α-Mn_2O_3, amorphous MnO_2, and hollandite α-MnO_2), which were unambiguously assigned by Raman spectroscopy and X-ray diffraction (XRD). Additional insight into the crystallization dynamics and the temperature evolution of lattice parameters, domain sizes, and crystal orientations was provided by XRD performed *in situ* during thermal annealing in either oxidizing or reducing atmosphere. The O_2 pressure during PLD played the major role with hetaerolite $Zn_xMn_{3-x}O_4$ films as well, primarily affecting the O stoichiometry in the crystalline phase and the Zn-to-Mn cationic population within tetrahedral and octahedral lattice sites (see the Raman spectra of Figure 2). Preliminary voltammetric tests, supported by *in operando* Raman spectroscopy and *post-mortem* structural and morphological characterization, provided indications about the impact of materials nanostructure on Mn electrochemistry and the complex phase transformations in aqueous electrolytes. Finally, PLD succeeded in growing Si thin films with a tailored degree of nanoporosity, nanocrystal distribution, and oxygen content in Ar+H_2 gas and in fabricating high-loading electrodes (~1 mg cm^{-2}) and Si–C nanocomposites for ASSBs. First-time charge-discharge tests carried out at the Helmholtz Institute Ulm (HIU) in solid-state lithium coin cells delivered promising electrochemical performances (e.g., ~1500 mAh g^{-1} over 30 cycles at 0.1 A g^{-1}), highlighting a trade-off between discharge capacity and cycling stability, in turn determined by the film nanomorphology (see Figure 3). Relying on a compelling materials science approach, this PhD work gave prominence to the fine morphological, compositional, phase, and structural nanoscale design achievable by PLD. Nonetheless, it also disclosed the intrinsic complexity of the synthesis process and the delicate interplay between deposition parameters and film properties, demanding future in-depth analysis in view of the optimization and practical implementation of advanced electrode materials.

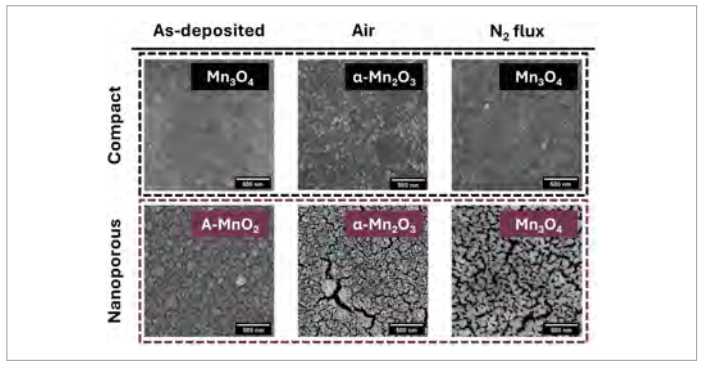

Fig.1 - SEM images of different Mn oxide phases, as a function of morphology and annealing atmosphere.

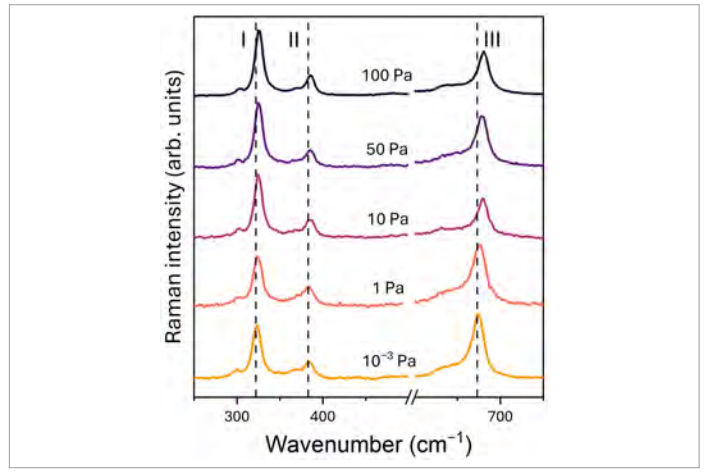

Fig.2 - Raman spectra of crystalline $Zn_xMn_{3-x}O_4$ thin films as a function of the oxygen deposition pressure.

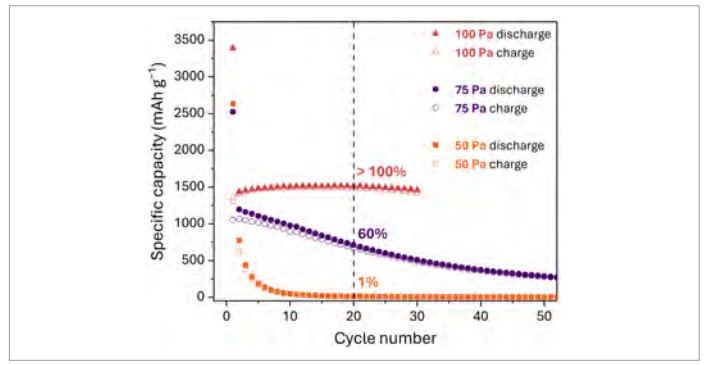

Fig.3 - Capacity retention of nanoporous Si thin films as a function of the Ar+H_2 deposition pressure, during charge-discharge tests at 0.1 A g^{-1}.

DESIGN, MODELLING AND TECHNO-ECONOMIC OPTIMIZATION OF TWO NOVEL OXY-COMBUSTION CYCLES

Matteo Martinelli - Supervisor: Emanuele Martelli

Tutor: Paolo Chiesa

In a global scenario where the reduction of greenhouse gas emissions is becoming a priority for the international community, the pressure on the energy sector to contribute to this common objective is increasing by the day. According to several studies, a crucial role to achieve a significant reduction in carbon dioxide emissions for power generation purposes is expected to be played by carbon capture and storage; among its possible applications, the one that has been proven to achieve the most promising preliminary results in terms of both emissions abatement and overall performance is oxy-combustion.

In this thesis, an accurate techno-economic analysis of two novel oxy-combustion cycles has been performed: on one side the Allam cycle, which has been gaining significant attentions in the past few years, thanks to its high efficiency, near-zero emissions and relatively low cost of the produced electricity; on the other side the Solid oxide semi-closed CO2 cycle (SOS-CO2), patented a few years ago by researchers of Politecnico di Milano. This cycle is expected to achieve unprecedented levels of net electric efficiency in the energy sector, due to the integration of a Solid Oxide Fuel Cell (SOFC) with a CO2-based bottoming regenerative Brayton cycle.

The two cycles have been accurately modelled, and the influence of all the main operating variables has been studied in detail, with the double objective of finding the optimal values of such variables and identifying technical criticalities. Then, the results of the analysis, together with considerations on the technical feasibility of the main cycles components and indication from an ongoing experimental testing campaign on the SOFCs, have been used to identify a preliminary design of the cycles, with particular focus on the SOS-CO2 cycle, given the absolute lack of literature information on such a novel cycle. For this purpose, two detailed models were developed ad-hoc for the evaluation of two of the main components of the cycles: the regenerator and the expander. Thanks to these models it was possible to perform a detailed preliminary sizing and design of the components, providing very useful information to assess and improve the quality of the overall cycle performance, both in terms of net electric efficiency and economic performance.

The results have shown how the Allam cycle, operating under extremely conservative assumptions, is still able to reach an efficiency of 53.2% for a 400 MW power plant. Moreover, it was confirmed that the cycle operates at the highest efficiency by providing oxygen as pure as possible from the ASU (99.5%). In addition, the results of the sensitivity analyses have also shown how the cycle is strongly dependent on the heat integration with the ASU: the efficiency drops to 50.1% if such integration is removed. The numbers also pointed out how additional medium-low temperature waste heat could be recovered in the regenerator with a high marginal conversion efficiency (35% for double the amount of heat of the ASU main air compressor intercooler), bringing the overall cycle net electric efficiency to 56.1%. In terms of size of the plant, the Allam cycle has shown a slow efficiency reduction with the size up to 100 MW (51.8%), while the adoption of an uncooled expander for smaller plants makes the efficiency drop to 48.7%. As far as the SOS-CO2 cycle is concerned, this study confirmed very high efficiency that can be reached even with uncooled expanders both in the supercritical version of the cycle (74.0%) and in the subcritical version (68.9%), a conservative alternative which could be realized in the next few years in terms of technical feasibility of the operating conditions. Both the cases featured the same plant size of the Allam base case of 400 MW. The main operating parameters of the subcritical version of the cycle have been studied (including the SOFC fuel utilization factor, voltage and operating pressure, the purity of the oxygen provided by the ASU and the minimum cycle pressure), selecting the best possible values according to the evaluation of both sensitivity analysis and practical issues generated in the cycle simulation and experimental campaign on the SOFCs. The efficiency of the SOS-CO2 cycle was found to be even less size-sensitive than the Allam cycle: ranging from 400 MW to 50 MW it drops from 68.9% to 67.2%.

In terms of economic performance, the analysis has shown how the Allam cycle benefits from a lower specific capital cost with respect to both the NGCC with post combustion capture and the SOS-CO2 cycle (2572 vs 3089 vs 3761 €/kW, respectively). On the other hand, the high efficiency of the SOS-CO2 cycle more than compensates for the higher capital costs if the natural gas cost reaches values above 12 €/GJ, for an assumed SOFC module cost of 1300 $/kW. Both the oxy-combustion cycles appear to be better alternatives than the NGCC over a wide range of natural gas costs (6-30 €/GJ), also thanks to the lower CO2 emissions (3.5 for the Allam vs 8.6 for the SOS-CO2 vs 38.61 g/kWh for the NGCC). Thanks to its higher efficiency, the economic advantage of the SOS-CO2 cycle increases with the fuel cost. Moreover, the Allam cycle turns out to be more sensitive to the cost of the turbine and recuperator, which represents a significant element of volatility due to the novelty of the components. As far as the size effect is concerned, when the cycle size decreases until 50 MW, the specific investment costs of the two cycles become similar, thanks to the modularity of the fuel cells that decouples the cost from the size, unlike what happens with the turbomachines and heat exchangers. In terms of COE, the economic analysis indicates that the 400 MW SOS-CO2 and the Allam cycles have similar values due to the combination of the differences in investment cost and efficiency (128.7 vs 128.8 €/MWh, vs 141.1 €/MWh for the NGCC). However, the smaller the size, the more the SOS-CO2 cycle increases its advantage.

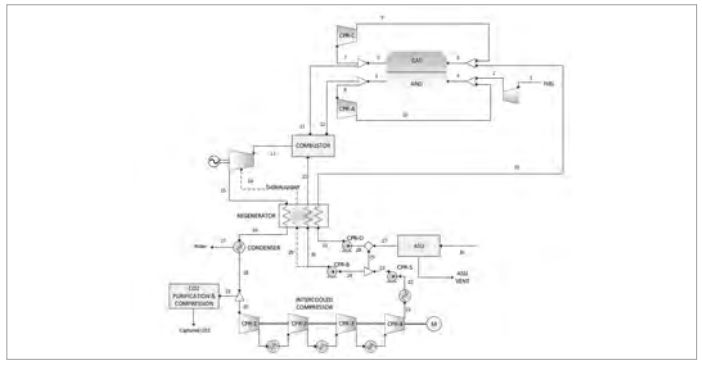

Fig.1 - Scheme of the basic layout of the SOS-CO2 cycle (supercritical configuration).

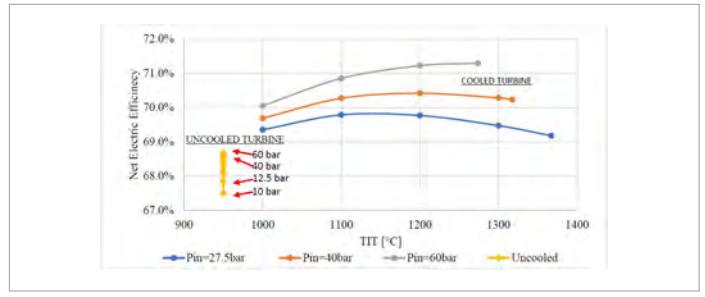

Fig.2 - Plot of the net electric efficiency as a function of the turbine inlet temperature and turbine inlet pressure for the SOS-CO2 cycle.

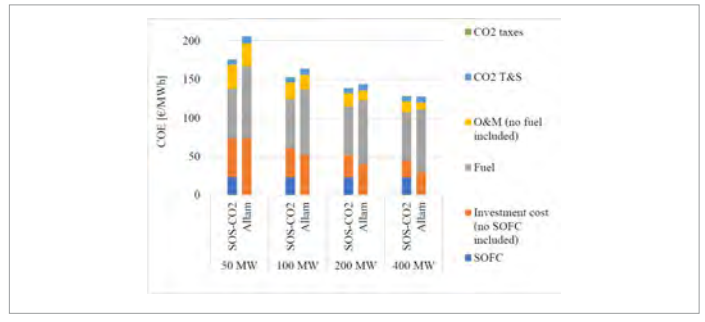

Fig.3 - Detailed composition of the COE for the all the considered cases.

SCENARIO ANALYSIS OF INTEGRATED ROAD-POWER INFRASTRUCTURES WITH HYBRID FLEETS OF ELECTRIC VEHICLES (EVS) AND INTERNAL COMBUSTION VEHICLES (ICVS)

Lida Naseh Moghanlou - Supervisors: Francesco Di Maio, Enrico Zio

Electric Vehicles (EVs) are key contributors to the reduction of CO2 emissions. However, EVs penetration poses new challenges for road networks design, operation and management, given that these have been conceived for Internal Combustion Vehicles (ICVs). A transition to EVs necessitates ensuring that the integrated road-power infrastructure can sustain mobility effectively, even in case of disruption due to car accidents or disturbances due to traffic jams, with respect to the road infrastructure, and loss of power supply, with respect to the power infrastructure.
This PhD thesis illustrates the conception and development of a scenario analysis framework, as shown in Figure 1, to study the impact of EVs penetration, under car accident conditions. The framework allows modelling the System of Systems (SoSs) comprised by road network, electric power system and vehicles. Graph Theory is used for describing the topological structures of the road and power systems. Finite State Machine (FSM) and Cell Transmission Model (CTM) are compared with respect to the modelling of the dynamic motion and state transition of vehicles within the road network. Finally, a metric is originally proposed to quantify the economic service losses related to delays that vehicles may incur in different accidental scenarios, and the resulting transport reliability of the overall SoSs.

The framework is applied on a benchmark road-power infrastructure travelled by a mixed fleet of EVs and ICVs. Different EVs penetration levels are considered.
The results show that the SoSs framework allows conducting meaningful analysis of the suitability of an existing road-power infrastructure to sustain the penetration of EVs. As such, it can be a valuable tool for design, operation and management: it can allow the decision-makers comparing alternative road-power infrastructure designs (e.g., critical roads, optimal gas and charging station locations, power network structure and topology, ...) in relation to potential economic service losses and transport reliability. From the methods point of view, FMS is shown to capture effectively, more than CTM, the effects of disruptions, at the expenses of a larger computational cost compared to CTM.

Keywords: Electric vehicle (EV) Internal combustion vehicle (ICV), Road network, Power network, System of systems (SoSs), Transport Reliability (TR), Service Loss, scenario analysis, Accident scenarios, Single-vehicle model, Flow-vehicle model, Finite State Machine (FSM), Cell Transmission Model (CTM).

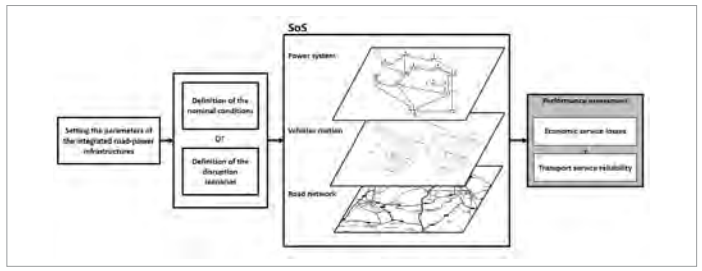

Fig.1 - Schematic representation of the framework for the analysis of integrated road-power network.

PHYSICO-CHEMICAL INVESTIGATION OF AL_2O_3 SEQUENTIAL INFILTRATION SYNTHESIS INTO DIFFERENT POLYMERIC MATRICES

Alessia Motta - Supervisor: Michele Perego

Tutor: Carlo Spartaco Casari

Organic-inorganic hybrid materials are highly attractive in a variety of applications due to their unique structure and properties, as they combine both inorganic and organic characteristics. Currently, these materials are synthesized using liquid-phase methods, which present several limitations. To address these constraints, vapor phase methods have emerged as a promising alternative. Among them Sequential Infiltration Synthesis (SIS) is an emerging vapor-phase technique for creating organic-inorganic hybrid materials and/or inorganic nanostructures from a suitable polymer template. In SIS, an organic matrix is alternately exposed to a metalorganic precursor and a co-precursor, with the exposure steps separated by a purge in an inert gas flux to remove unreacted molecules and reaction by-products. The pulse/exposure/purge sequence is illustrated in Figure 1a, while Figure 1b depicts the sample structure after the SIS process. The SIS process results in a thin inorganic film coating on the substrate surface, along with the formation of an organic-inorganic hybrid layer (Figure 1b). The SIS mechanism is governed by complex physico-chemical phenomena, including precursor sorption, diffusion, and entrapment within the polymer matrix. These phenomena are interdependent, and they are influenced by both operational parameters and intrinsic material properties. A deeper understanding of the fundamental kinetics and thermodynamics governing SIS is crucial to expanding the range of materials that can be synthesized and broadening their technological applications.

This doctoral thesis investigates the underlying phenomena of SIS by infiltrating Al_2O_3 into various polymeric matrices using trimethylaluminum (TMA) and water (H_2O) as precursor and co-precursor, respectively. First, the effect of temperature (70–110 °C) on precursor diffusion is examined in the well-established poly(methyl methacrylate) (PMMA) system through *operando* spectroscopic ellipsometry (SE). This technique enables real-time monitoring of thickness evolution and optical property variations during the SIS process at different operating temperatures. By analyzing the first SIS cycles, the TMA diffusion coefficient (D) as a function of temperature and the activation energy (ED) for TMA diffusion into PMMA are extracted. The measured ED for TMA into PMMA is significantly higher than reported values for nonreacting molecules of comparable size in the same systems. This finding supports the hypothesis that the diffusion process is limited by the interaction of TMA with the reactive site of the PMMA. Moreover, intracycle analysis allows for a qualitative evaluation of the dependence of solubility and reactivity on the process temperature. The maximum mass uptake is observed at 80 °C. At this temperature the diffusivity is quite low, limiting the effective PMMA volume that could be infiltrated. However, at higher temperatures, TMA infiltrates deeper into the PMMA matrix, albeit with a lower mass uptake due to reduced reactivity at elevated temperatures.

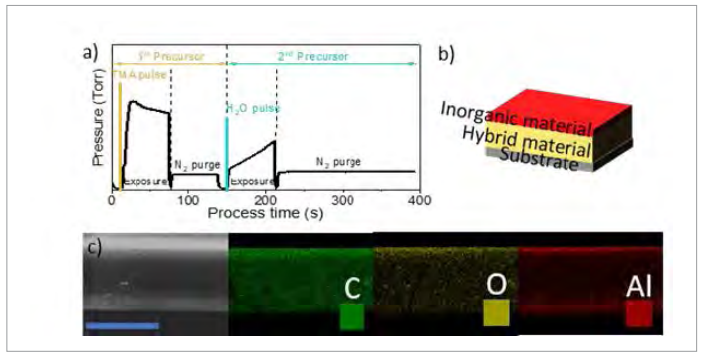

Fig.1 - a) Scheme depicting the experimental processing conditions for infiltration of Al_2O_3. b) Representative final hybrid materials structure and c) SEM and EDX elemental mapping of free-standing PBS samples following 25 SIS cycles.

Building on these insights, Al_2O_3 infiltration is extended to new polymer systems at a fixed temperature of 70 °C. The selected polymers—poly(butyl succinate) (PBS), poly(lactic acid) (PLA), and poly(butylene adipate terephthalate) (PBAT)—are bio-based, biodegradable polyesters characterized by ester functionalities positioned at different locations along the polymer chains. The Al_2O_3 SIS process in PMMA serves as a reference. The kinetics and thermodynamics of the first SIS cycle are investigated using *operando* SE and ex situ X-ray photoelectron spectroscopy (XPS). During SIS, significant polymer swelling is observed due to precursor absorption and diffusion, followed by shrinkage during purging as unreacted TMA molecules diffuse out. O*perando* SE analysis reveals that all polyester films exhibit substantial swelling upon TMA exposure, whereas PMMA undergoes only moderate swelling and follows Fickian diffusion behavior. During the purging step, PMMA exhibits significant deswelling, while polyester matrices show only moderate deswelling. This behavior suggests that a larger faction of diffused TMA molecules can be effectively trapped inside the polyester matrices by chemical bond. Consistently, ex-situ XPS analysis demonstrates a higher amount of Al_2O_3 grown in the polyester polymers. The ex-situ XPS analysis reveals that the TMA incorporation occurs primary through the formation of Al-O covalent bond at the C-O-C group for all the tested polymers. Notably, the position of the reactive group plays a crucial role in the inorganic mass uptake: when ester groups are located in the polymer main chain, they facilitate chain cleavage, enhancing TMA diffusion and reactivity. Conversely, ester groups confined to side chains, as in PMMA, stabilize the polymer structure, restrict diffusion, and limit chain scission. These findings are leveraged to extend SIS applications to free-standing PBS membranes. Figure 1c presents representative images of PBS membranes post-infiltration, demonstrating uniform C, O, and Al distribution throughout the film thickness, indicative of high TMA diffusivity and reactivity in PBS.

Finally, the acquired knowledge on diffusion and entrapment is applied to fabricate functionalized inorganic nanostructures using hexagonally packed poly(styrene-block-methyl methacrylate) block copolymers as templates. The final dimensions of the inorganic structures are finely tuned at the nanoscale by SIS process parameters.

The findings of this thesis provide critical insights into the intricate mechanisms governing SIS. This work advances the fundamental understanding of the SIS process phenomena enabling precise control over inorganic materials growth within organic matrices and the development of hybrid materials with tailored properties. Moreover, by considering the thermodynamics and transport phenomena involved, this study paves the way for the extension of SIS beyond metal oxides to include functional nitrides, sulfides, and other advanced materials.

MODELLING MEMBRANE-BASED SYSTEMS FOR PROCESS INTENSIFICATION

Michele Ongis - Supervisor: Marco Binotti

Co-Supervisors: Gioele Di Marcoberardino, Fausto Gallucci

According to recent analyses, the European Union has to follow a path of joint decarbonization and growth of industrial competitiveness.
These two objectives are, however, historically in contrast: being a flare of climate responsibility might run contrary to competitiveness and growth.
Scientific research efforts focus on finding solutions for sustainable growth. Among them, one path is called *process intensification*, a general term meaning using innovations to enhance existing processes, reducing their energy intensity and, potentially, their cost.
A commentary article, published in Nature in 2016, titled *seven chemical separations to change the world*, suggested that avoiding thermal methods for purification of chemicals might save huge amounts of carbon dioxide emissions and costs. Membrane-based separation methods, in particular, were suggested as a game-changer technology.
This is the driver of this Thesis, which scope is the development of mathematical models to evaluate the techno-economical benefits of membrane-based separation alternatives in different applications, industrial sectors and technology readiness levels.
Membranes are thin barriers used for the selective separation of chemical components, and their low energy intensity, low cost and broad versatility make them a suitable alternative for almost all separation industries. The term *membrane* covers a large variety of materials, with many different properties and structures, and this is also true for *membrane processes*. Each process needs to be studied in great detail to assess which membrane, in which conditions, might represent a viable solution.
In membrane science, modelling activity is a fundamental support, both in the phase of model development, to study membrane features and reduce the need of expensive experiments, and for the techno-economic evaluation of the whole system, lending a hand to their industrial implementation.
This work is divided in three parts, each one in turn divided in two chapters: one about the development of a modelling tool, and the second about the techno-economic assessment of the membrane-based application, by using the tool developed.
Mathematical model development also includes the coding of customized blocks in Aspen Custom Modeler®, to have available unit operations exported in Aspen Plus®, where the processes were designed, optimized and their economics assessed.

Chapter 1 provides a background to the concepts of membranes, modelling and their role in process intensification.

PART 1 is about H_2 separation from a gaseous mixture using Pd-based membranes. It is divided in two chapters.
Chapter 2 is about the development of an analogous of ε-NTU method applied to mass exchangers (i.e. membrane modules). ε-NTU method is a well-known method for heat exchangers design, based on a dimensionless form of the constitutive equations. The same can, and had already, be applied to a mass exchanger for reverse osmosis, where it is named ε-MTU method. Effectiveness ε is the ratio between H_2 separated over the maximum amount of H_2 that can be separated through the membranes; MTU is an ad-hoc defined dimensionless number.
In this chapter, the method is developed for hydrogen separation in metallic membranes. It turned out a powerful tool to be used to have an a priori prediction of the performance of a membrane, in terms of hydrogen recovery from a gaseous mixture.
Chapter 3 investigates H_2 recovery from natural gas grid. The novelty of this study is about the insight in the design of the separation module, which optimization allows a reduction of the membrane area for H_2 recovery. Module optimization is possible thanks to the development of an empirical model to evaluate concentration polarization entity. Indeed, based on experimental results, a simple mathematical model of polarization is developed, based only on two parameters: inlet hydrogen molar fraction and effectiveness ε. The techno-economic assessment demonstrates that Pd-based membranes represent a viable solution for the deblending process. With a 10% blending, reference costs using PSA were around 7.64 €/kg, while results in this assessment were in all cases, even at lower grid pressures, below 4.44 €/kg, for the separation of 25 kg/day of pure hydrogen.

PART 2 is about H_2 production in a dense metallic membrane reactor. H_2 is produced from autothermal reforming of biogas and separated in the same fluidized bed reactor via immersed Pd-based membranes.
Chapter 4 introduces the performance charts: maps where the reactor behavior can be summarized. The charts have in y-axis the hydrogen recovery factor, which represents a combined efficiency in hydrogen production and separation, and in the x-axis the pure hydrogen production. Starting from design situation, the effect of all operating parameters is investigated, and the results are displayed to capture the complex reactor response. The charts allow also to support design stage of the reactor.
Chapter 5 makes a generalization of the performance charts, minimizing the variables to be investigated in the techno-economic evaluation. Reactor performance turns out to be expressed in terms of total membrane area, regardless of their distance, length and gas velocity. Generalized performance charts are the basis of the techno-economic assessment at system level, in a process of 100 kg/day hydrogen production from autothermal reforming of biogas. The performance of the MR-based solution is compared to the conventional process. Thanks to the in-unit separation, the MR can substantially reduce the operating temperature to about 500 °C, in the region compatible with the membranes' operation. Production cost of hydrogen turned out to be convenient compared to benchmark solution. For H_2 production at 20 bar, levelized cost resulted 6.81 €/kg for the MR-based solution against 7.31 €/kg estimated for the benchmark.

PART 3 is about polymeric membrane application in biotechnology, in the process of ω3 fatty acids enrichment in fish oil. In this concentration process, a selective lipase detaches preferentially, from triacylglycerols that compose fish oil, the short-chain fatty acids, leaving the ω3 attached to the glycerol backbone. Subsequently, the membrane separates preferentially the detached esters, retaining a mixture enriched in ω3, that represents the final product.
Chapter 6 is about a refinement of the macro-kinetic transesterification model compared to scientific literature. Former models assumed that any glyceride has only one type of acid attached. This assumption had the limitation to overestimated triglycerides and underestimate di- and mono-glycerides. The new formulation of the model assumes a uniform distribution of the acids on the available positions and it is compared to the former model by fitting the same experimental results. The random description is likely to mitigate the problem of the former model, and it is therefore recommended whenever a detailed description of the glyceride fraction is required.
Chapter 7 integrates the newly developed kinetic model into the techno-economic comparison of the membrane-based system against the conventional route for fatty acids enrichment. In this chapter, permeation mechanism has been modelled through experimental determinations of different components' permeabilities. In a 10 L/h production plant, membrane-based process is able to enrich the oil from 31.65% up to 54% (a factor 1.7). The products cost ranges from 13 €/kg at low enrichment up to 33.2 €/kg at 1.7, outperforming the results of the benchmark solution, from 16.5 €/kg to 39.2 €/kg in the same range.

Chapter 8 gives the general conclusions of the work: it is confirmed that membrane-based technologies have the potential to substantially intensify different processes, and modelling activity represents a fundamental support for this transition. Modelling tools development is therefore highly encouraged.

DEVELOPMENT OF NANOSTRUCTURED MATERIALS FOR HIGH INTENSITY LASER-PLASMA APPLICATION

Davide Orecchia - Supervisor: Matteo Passoni

Co-Supervisor: Alessandro Maffini

The field of laser-matter and laser-plasma interaction is gaining increasing interest from the scientific community in recent years, owing to the multiple applications of great scientific, technological, and societal impact. At the same time, the scientific and technological complexity inherent in laser-matter and laser-plasma interaction cannot be overstated, particularly for the most demanding applications—that indeed are those with the highest societal impact, such as nuclear fusion or oncological hadrontherapy. In all of these, the coupling between laser and matter is a fundamental aspect, and its enhancement can be the key to reaching technological viability. In order to do so, near-critical density and nanostructured materials are gaining increasing interest as laser-facing components, with very promising results. A specific influence of the nanostructure morphology on the laser-matter interaction process has also been demonstrated, highlighting the need for a proper design and control of the nanostructured targets. At the same time, the great variety of regimes of interest should be considered—tabletop or high-intensity lasers, ultrashort pulses or high energy nanosecond pulses—each with its own target requirement for optimal laser-matter coupling. Currently exploited material science techniques to obtain nanostructured materials present significant limitations in this regard: chemical methods can have difficulties in controlling the material structure down to the nanoscale, their versatility is limited, and unwanted byproducts may be present. A physical vapor deposition technique such as Pulsed Laser Deposition (PLD) can address many of these limitations, as a bottom-up approach with potentially great nanostructure control, stoichiometric growth capabilities and great flexibility thanks to the many tunable process parameters. Among those, the laser pulse duration is not often considered: while nanosecond lasers are routinely part of PLD systems (ns-PLD), ultrafast ablation with femtosecond lasers—in the much less explored fs-PLD approach—could provide an even greater versatility, due to the electronic ablation mechanism and direct nanoparticle production.

The first part of this PhD work is devoted to an in-depth investigation of carbon nanofoam production through ns and fs-PLD, with the aim to determine how the macroscopic material properties—such as density and uniformity—are influenced by the main deposition parameters, and how they can be connected to the properties of the fractal aggregates produced during the aggregation process. Still toward the same aim, the analysis is then expanded to other elements (B, Si, Cu, W and Au), exploiting the flexibility of the fs-PLD technique. The morphology evolution is similar in all cases, from nanoparticle-assembled films in vacuum to tree-like morphologies and finally nanofoams at higher pressures. The film average density, in great part a consequence of its morphology, follows an analogous trend, with a sharp decrease in correspondence to the main morphological transition. The differences among the elements can be explained through a simple model of the background gas slowing effect, where the nanoparticles size and density (along with the background pressure) are the main driving parameters.

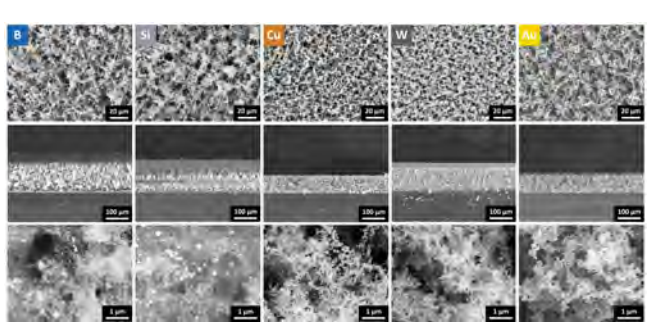

Fig.1 - Nanofoams of different elements (B, Si, Cu, W and Au) produced through fs-PLD (from top to bottom: plane view, cross-section and details).

The results of this detailed investigation were then put to use toward the last aim: the design and production of nanofoam-based targets, and their test in application-oriented laser-driven experimental campaigns. The first one is performed in collaboration with CLPU (Centro de Laseres Pulsados in Salamanca), on the petawatt-class laser Vega 3, in the framework of laser-driven particle acceleration. Carbon nanofoam-based double-layer targets (DLTs) have been successfully exploited to enhance proton acceleration performances, combining freestanding thin aluminum substrates (obtained with magnetron sputtering) with carbon nanofoams produced through ns-PLD. The experimental test of the DLTs highlighted the great importance of both target and holder design, especially considering the damage to the foam layer in higher repetition rate operation. The second potential application, related to the use of carbon nanofoams as ablators in inertial confinement fusion, is investigated in collaboration with ENEA Frascati, hosting the high-energy nanosecond duration ABC laser. Preliminary hydrodynamic simulations on the MULTI-FM code are also performed, with the aim of defining the range of optimal target parameters (in terms of morphology, density and thickness) to enhance laser absorption. The experimental activity performed gave particularly promising results for the overcritical tree-like carbon foams, which showed increased laser energy absorption and improved ablation loading as demonstrated by a higher ablation crater volume. Interestingly, lower density carbon nanofoams appeared transparent to the laser, despite the overcritical average density, likely due to the foam porous structure (not light-tight). Lastly, in the framework of proton-boron fusion research, the potential of fs-PLD is fulfilled in the production of hydrogen-enriched boron nanofoam targets, by codeposition of boron and HDPE. The targets are tested on the Taranis laser (high intensity, picosecond pulse duration) at Queen's University Belfast. A significant enhancement of the alpha particle yield was demonstrated for the mixed B-CH nanofoam targets, when compared to boron nanofoams or boron nitride compact targets. Moreover, the data support the interpretation of fusion reactions occurring in the foam, with a possible contribution due to the ions accelerated by Coulomb explosion of the nanoparticles. As a last remark, it is worthwhile to consider that the three experiments were performed on quite different laser systems, each leading to distinct optimal target properties, highlighting the importance of a versatile technique for target production in laser-matter interaction applications.

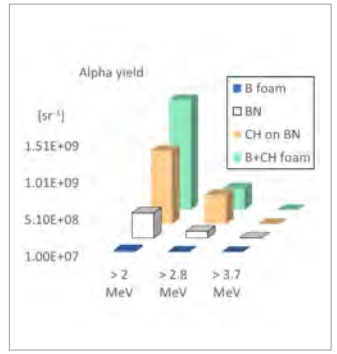

Fig.2 - Alpha particle yield enhancement in hydrogen-enriched boron nanofoam targets.

EXPERIMENTAL AND NUMERICAL ANALYSIS OF TWO-PHASE FLOW IN CHEVRON-TYPE CORRUGATED CHANNELS

Stefano Passoni - Supervisor: Ricardo Mereu

Plate Heat Exchangers (PHEs) gained widespread recognition in the industrial sector due to their efficiency and compact design. They consisted of a pack of gasketed or brazed corrugated plates that enhanced heat transfer by promoting mixing and turbulence on both the hot and cold sides. The primary advantage of PHEs lay in their high performance relative to their compactness, demonstrating greater efficiency than shell and tube or other standard industry heat exchangers. Historically, gasketed PHEs were used exclusively for single-phase applications in industries such as dairy, food, and chemicals. From the mid-1980s, their application expanded to heating, ventilation, air conditioning, and refrigeration (HVAC&R) thanks to the advent of brazed and semi-welded PHEs. More recently, compact plate heat exchangers have been considered for use as steam generators in Small Modular Nuclear Reactors (SMRs), where the size limitations of standard shell and tube heat exchangers posed a challenge. As a result, increasing industrial and scientific interest focused on studying two-phase flows within these components.

This thesis investigated the fluid-dynamic behavior of chevron-type corrugated channels commonly used in plate heat exchangers, focusing on a two-phase adiabatic air-water mixture as the working fluid. An innovative experimental setup was developed, featuring a 1:1 transparent replica of a commercial steel plate to simulate internal fluid dynamics while allowing flow visualization through high-frame-rate videography. This approach enabled the precise identification and documentation of flow patterns, leading to the definition of six distinct flow patterns: fine and coarse bubbly flow, Taylor-like bubbly flow, heterogeneous flow, partial film flow, and fully developed film flow. The results were synthesized into a global flow regime map that integrated findings from previous studies with those from this research. The empirical data generally aligned with documented flow patterns, with deviations arising from subjective visual categorization and different experimental configurations.

To further utilize the extensive data captured in high-speed videos, the study introduced a methodology that combined machine learning (ML) algorithms with data processing techniques for post-processing back-lit front-view HSV images of two-phase flow within the corrugated channel to estimate the void fraction. The U-Net architecture was used for semantic image segmentation to distinguish between gas and liquid phases. After progressive training with image sets of increasing complexity, the network produced highly accurate binary masks, with standard performance metrics scoring above 90%. A novel algorithm was developed to reconstruct 3D gas cluster volumes from 2D binary masks, improving void fraction estimation as a volume ratio. A drift flux model was proposed to fit the dataset, with a two-part equation introduced to account for the dependence of the distribution coefficient C_0 on the liquid flow rate for a corrugation Froude number $Fr_{\sim}$ larger than 1. Additionally, dimensional parameters extracted from the binary masks were used to establish quantitative criteria for flow regime transitions.

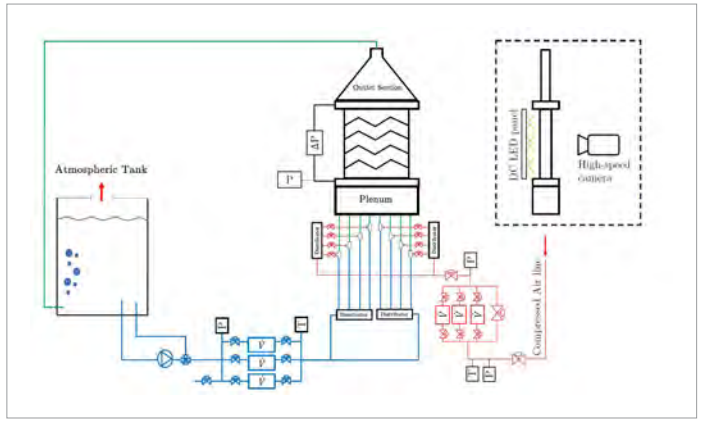

Fig.1 - Scheme of the experimental loop used for experiments and detail of the setup used for flow visualization.

Beyond providing insights into the fluid dynamics and flow regimes inside the corrugated channel, the experimental campaign enhanced the understanding of pressure drops in both single-phase and two-phase flows. Pressure drop measurements were conducted, and for single-phase flow, a dimensionless analysis was performed, leading to a novel correlation for Darcy's friction factor. Two-phase pressure drops were represented using two-phase multipliers on a Lockhart-Martinelli chart. The void fraction model obtained from image analysis outperformed the homogeneous flow assumption in computing the gravitational component of the two-phase pressure drop, leading to a better representation of the frictional term. This resulted in less scattered and more accurately correlated data, significantly improving the accuracy of the two-phase pressure drop model.

The final stage of the fluid dynamic analysis of the cross-corrugated channel involved Computational Fluid Dynamics (CFD) simulations. While simulations provided several advantages over experimental methods, both approaches were complementary, as a benchmark was required to assess the accuracy of the simulations. A grid sensitivity analysis was conducted to identify critical parameters for computational grid construction, with the maximum cell dimension proving particularly influential. The implicit Volume Of Fluid (VOF) method was employed due to its sharp interface tracking capabilities and computational efficiency. The simulations produced correlations for single-phase friction factors and two-phase multipliers, a drift flux model for void fraction distribution, and numerical flow visualizations. The results showed that simulations were a valuable tool for analyzing multiphase flow inside corrugated channels. The single-phase friction factor tended to underestimate experimental data, leading to an overall overestimation of the two-phase multiplier. However, void fraction modeling and numerical flow regime visualization demonstrated high accuracy, effectively replicating the experimentally observed flow patterns.

In conclusion, this research established a foundation for further studies on multiphase fluid dynamics inside corrugated channels. Future work may investigate the effects of corrugation parameters, such as angle and depth, on flow regimes and pressure drops through a parametric study that builds upon and refines the methodology proposed in this thesis. Additionally, the impact of operating pressure on fluid dynamics remains an open research topic, as no existing literature addresses this aspect.

OPTIMAL DESIGN AND OPERATION OF AGGREGATED ENERGY SYSTEMS

Lorenzo Pilotti - Supervisor: Emanuele Martelli

Co-Supervisor: Giampaolo Manzolini - Tutor: Paolo Chiesa

Aggregated Energy Systems (AES), such as Multi-Energy Systems (MES), Virtual Power Plants (VPP) and microgrids, are emerging as promising solutions in the energy landscape, particularly regarding the aspect of distributed generation, because of their capability to integrate and combine conventional and renewable technologies to increase the renewable penetration in the system, and at the same time, achieve better technical, economic, and environmental performance with respect to non-aggregated solutions.

However, the development of such systems may be hindered by the higher level of complexity associated with AES design and management in comparison to traditional, centralized plants, often consisting of a single technological solution. If not carefully designed and wisely operated, the full integration potential can not be unlocked, with the risk of offsetting part of the benefits arising from the additional flexibility offered by highly integrated systems. Therefore, rigorous modelling tools based on a solid mathematical theory should be developed to support the complex decision-making process that characterizes the AES design and operation.

In this thesis a comprehensive and flexible optimization framework for the optimization of the design and operation of AES is proposed. The aim of the developed methodology is to identify a preliminary but sufficiently robust optimal design of aggregated systems able to consider the uncertainty, both in input parameters and in the energy supply. To do so, the preliminary system operation should be included in the design problem, leading to the formulation of a complex two-stage stochastic multi-period optimization problem: in the design stage, where the decisions on type, numbers and sizes of units are made and the operation stage, where the optimal scheduling of the units configuration previously selected is evaluated. The objective of the operation stage is to provide a preliminary plant schedule to (i) correctly estimate all the operating costs and (ii) design a flexible system able to face any operating condition (i.e., robust with respect different realizations of the uncertain parameters).

Since input-output constitutive relationships, performance maps and the scale effect on the investment cost and nominal performance of components are intrinsically nonlinear, linearization procedures are incorporated into the optimization model so that the resulting optimization problem can be formulated as a Mixed Integer Linear Program (MILP) that can be efficiently solved by state-of-the-art linear solvers, such as CPLEX and Gurobi. Because the need to consider long-term time horizons, typical of investment planning problems, tackling simultaneously the problem of design and operation of AES is very challenging even for modern solvers and often results in a large-scale MILP. For this reason, to reduce the problem size and contain the temporal dimension of the optimization horizon, a limited number of representative periods are selected as operational scenarios of the optimization problem by means of data aggregation and clustering techniques.

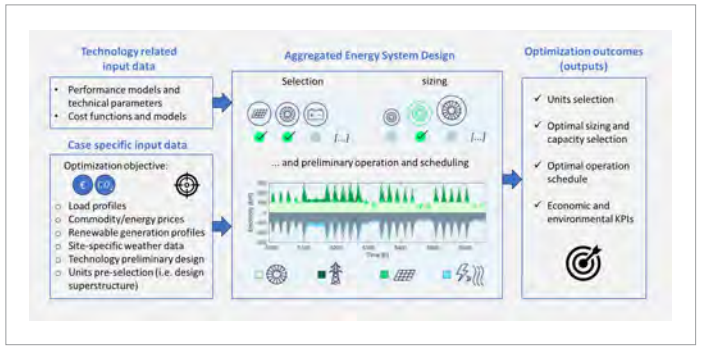

Fig.1 - Schematic representation of the optimization framework developed.

In order to apply the proposed methodology to complex real-world problems, several approaches for AES design, resulting in different MILP formulations, are compared with each other and the most computationally efficient formulation is identified. Subsequently, to further reduce the computational time and speed-up the solution process, two decomposition algorithms exploiting the two-stage structure of the problem have been incorporated into the optimization framework and successfully applied to solve large-scale problems.

Subsequently, to validate the optimization framework developed in this thesis and demonstrate the flexibility and the full spectrum of its optimization capabilities, five possible real-world applications are shown in this thesis. The first case study regards the design of a microgrid including an Electric Vehicles (EVs) charging station, Photovoltaic (PV) panels, and a battery storage to cover EVs charging requirements and to supply the electrical load of an industrial site nearby. The additional flexibility offered by Vehicle-to-Grid (V2G) capability of EVs is investigated and the potential interactions of the systems with the Italian national energy markets are assessed. To this purpose, a detailed description of the Italian Ancillary Services Market (ASM) has been integrated within the optimization framework for the accurate modelling of the ASM markets (primary, secondary and tertiary reserve). In order to properly validate the proposed sizing methodology, the optimized design is compared with the one obtained with traditional sizing methodologies and the benefits of the a rigorous mathematical approach are shown.

The second example of application is the design of a CSP plant hybridized with other renewable technologies (i.e., PV and wind). Several design configurations to cover entirely or part of the national electricity demand are explored and compared with their respective standalone solutions to show the benefits of technology hybridization.

The third case study consists in the optimization of a fully renewable AES equipped with two long-term storage solutions to shift the seasonal variations in the renewable production: a Battery Energy Storage System (BESS) for stationary energy storage and a Power-to-Power (P2P) that relies on hydrogen storage. The system design is optimized to cover a fraction of the electricity demand of the Sicily region, in the South of Italy. The techno-economic feasibility of the plant is evaluated under two different scenarios (current and future), to estimate the impact of technology efficiency improvements and cost reductions.

The mathematical model is then applied to the design of an industrial chemical facility for the co-production of blue hydrogen and power. Also in this case, the economic and environmental benefits of the polygeneration system are demonstrated against the separated production of the two energy commodities (electricity and hydrogen).

Finally, the design optimization of an off-grid microgrid to supply an LNG plant and a medium-size airport with high reliability requirements is reported. To cover the electrical load, the AES is composed of several Gas Turbines (GTs) integrated with PV generation and BESS for backup power.

Give the high level of reliability characterizing the off-grid system, reserve constraints are added to the optimization model to provide the required power while always keeping a reserve margin and also to select a spare turbine for backup in case of failure of one of the running GTs.

In conclusion, the results in all the reported applications proven the effectiveness of the proposed design optimization methodology in identifying the optimal, reliable and robust design of many AES, even when dealing with real-world complex problems. This further motivates the continuous improvements of the optimization framework by considering other aspects that may influence the accuracy of design outcomes (e.g., including system topology or allowing for multi-stage investments) and by further reducing the computational times (e.g., developing tailored and ad-hoc solution techniques).

DEVELOPMENT OF AN INTEGRATED MODELLING FRAMEWORK TO ASSESS ENVIRONMENTAL, ENERGY-SECURITY- AND ECONOMIC IMPLICATIONS OF GLOBAL ENERGY TRANSITION SCENARIOS

Lorenzo Rinaldi - Supervisor: Matteo Vincenzo Rocco

In recent years, the need to undertake an energy transition has been increasingly prominent in the political debate and the effects of such an ongoing transition are leading to increasing global energy investments. The switch to the vast adoption of low-carbon technologies would lead to less environmentally-impactful energy production processes, however, it surely requires structural economic changes in terms of global supply chains. In particular, the concern around such technologies regards their relevant critical raw materials (CRMs) content, which consequently opens important geopolitical and energy security implications, and their role in global job creation/loss. These two dimensions are currently under investigation in the scientific literature and a comprehensive answer represents a substantial research gap. Such a complex context needs to be represented within complex and integrated modelling frameworks. Energy System Models (ESMs) are usually the favourite choice when dealing with the impact evaluation of long-term global energy scenarios. However, it is necessary to create a link between ESM and other macroeconomic tools to keep into account the above-mentioned complexities. This is the purpose of DYNERIO, an integrated modelling framework developed by the authors, composed of three soft-linked modules: (i) an ESM, responsible for optimizing sustainable technological pathways under specific policies constraints, usually minimizing the least total net present cost (NPC) of the energy system configuration; (ii) a multi-regional input-output (MRIO) model, reflecting results of ESM onto non-energy industries and capturing the overall economic impact, including influence on employment, of the pathway; (iii) a third module consisting of a system of linear equations allowing to dynamically assess region- and technology-related CRMs extraction and recycling (dynER). This thesis undergoes two applications of the DYNERIO framework within an extended global energy transition case study aiming at providing extended energy-related and economic insights. Two global energy scenarios have been implemented in the ESM: the first provides a least-NPC-oriented transition trajectory shaped under policy constraints classifiable as "stated and announced"; the second scenario builds upon the first with the significant difference regarding the relaxation of some policy constraints and the change of the objective function of the ESM, which in this case is the minimization of the total CO2 emissions. Capacity deployments and energy production mixes are then exchanged to the MRIO and dynER modules in a soft-linked approach in both cases study. The first case study deals with global energy transition and its environmental impacts in terms of emissions and CRM exploitation and recycling. The second investigates the potential for decarbonization in the steel industry in the European Union, keeping an eye on multi-regional considerations. Both applications show how an integrated soft-linking between these modules can be effective in describing multifaceted aspects of the transition, distinguishing among the different outputs and uncertainties brought by the use of different databases and structural assumptions.

CFD COMBUSTION MODELING OF ALTERNATIVE FUELS WITH TABULATED KINETICS

Andrea Schirru - Supervisor: Tommaso Lucchini, Marco Mehl

Co-Supervisor: Angelo Onorati

The present PhD research was conducted as a joint collaboration between the CRECK Modeling Group and the ICE Group at Politecnico di Milano, aiming to advance the numerical modeling of internal combustion engines (ICEs) operating with alternative fuels. The study focuses on the development, validation, and application of tabulated combustion models to enhance computational efficiency and flexibility compared to conventional approaches.

Development of a Lookup Table Generator for Tabulated Kinetics

One of the key contributions of this research is the development of a new methodology for generating lookup tables within the OpenSMOKE++ framework. This approach enables the efficient representation of complex reacting flows while maintaining computational affordability. The lookup table methodology leverages precomputed kinetic solutions, significantly reducing the cost of solving chemistry in CFD simulations. The proposed framework improves the adaptability of combustion models to different fuels and operating conditions, making it a versatile tool for ICE simulations.

Validation of the Tabulated Combustion Models

The accuracy and robustness of the developed models were extensively validated against experimental data for single-fuel and dual-fuel configurations. In the single-fuel case, combustion simulations were performed using dimethyl ether (DME), a promising alternative fuel due to its high cetane number and clean-burning properties. The models were validated across different engine combustion modes, including Mixing-Controlled Compression Ignition (MCCI) and Late-Premixed Compression Ignition (L-PCCI), demonstrating excellent agreement with experimental results.

In dual-fuel applications, the tabulated models were extended to simulate Diesel-Hydrogen and Diesel-Ammonia combustion, capturing the complex turbulence-chemistry interactions involved in these systems. A dedicated lookup table was introduced to handle pilot-main injection conditions, effectively representing the reactivity stratification observed in dual-fuel combustion.

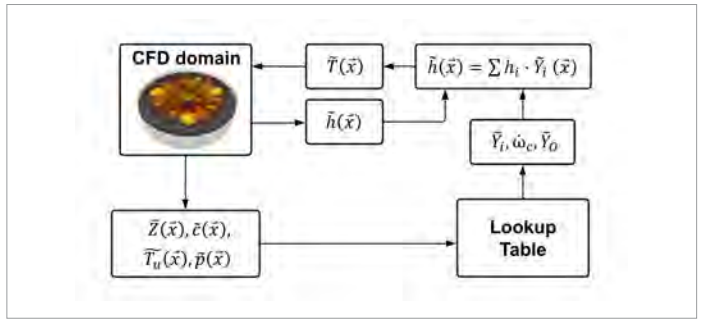

Fig.1 - Working principle of the Tabulated well-mixed (TWM) combustion model.

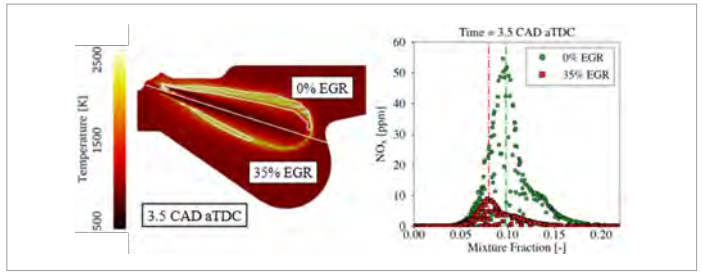

Fig.2 - Effect of Exhaust Gas Recirculation (EGR) on NOx formation in MCCI and L-PCCI combustion.

Impact and Outlook

The results of this research confirm the effectiveness of tabulated combustion models in simulating advanced combustion strategies for alternative fuels. The validated models provide a computationally-efficient toolset for engine developers seeking to optimize ICE operation while reducing pollutant emissions. Future developments will focus on expanding tabulation methodologies to cover additional low-temperature combustion (LTC) regimes and extending validation to industrial-scale applications.

Keywords: Alternative Fuels, Compression-Ignition Engine, Dimethyl Ether, Hydrogen, Ammonia, OpenFOAM, OpenSMOKE++, CFD.

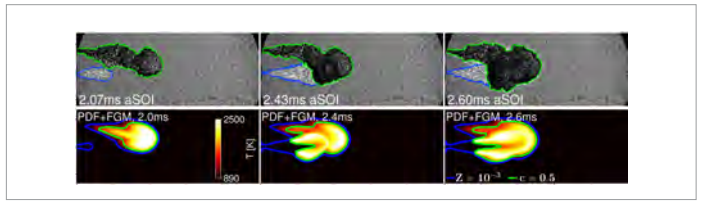

Fig.3 - Experimental vs. simulated flame morphology in dual-fuel Diesel-Hydrogen combustion.

DESIGN, PROCESS INTEGRATION AND OPTIMIZATION OF CO_2 PURIFICATION UNITS FOR CO_2 CAPTURE AND STORAGE APPLICATIONS

Syed Ali Zaryab - Supervisor: Emanuele Martelli

Co-Supervisor: Matteo Romano

The Earth's climate is rapidly changing due to human-caused greenhouse gas emissions, necessitating urgent action. Carbon capture and storage (CCS) technologies are crucial for mitigating these effects. These technologies capture CO_2 from industrial sources, after which the CO_2 is transported and safely stored underground. Various capture methods, including pre-combustion, post-combustion, and oxy-combustion, exist, each with unique advantages and challenges. However, the captured CO_2 stream typically contains O_2, N_2, and Ar at concentrations unsuitable for the stringent purity standards required for storage or transport. Therefore, a CO_2 purification unit (CPU) is required to reduce these impurities and increase CO_2 purity. Furthermore, purifying the captured CO_2 with a CPU allows the CCS process to operate at a lower purity and higher recovery point, potentially reducing emission costs. This PhD research focuses on the selection, design, modeling, process integration, and technoeconomic optimization of cryogenic CPUs for CCS applications.

This research investigated two main categories of CPUs: flash separation-based CPUs and stripping/distillation-based CPUs. Within these categories, six distinct CPU configurations were selected for detailed analysis. These configurations comprised: a fundamental flash separation unit, an enhanced flash unit augmented with a supplemental compressor, a distillation-based system, and three hybrid flash-distillation designs, each characterized by unique operational and optimization parameters. Subsequently, these selected CPU configurations were modelled using the Aspen Plus process simulation software.

A crucial step in simulating and modelling of a CPU involves selecting an accurate equation of state (EoS) to model the vapor-liquid equilibrium (VLE) behaviour of the CO_2 capture system. Thus, in this work several EoS, including Peng-Robinson (PR), Lee-Kesler-Plöcker (LK-Plock), Soave-Redlich-Kwong (SRK), Benedict-Webb-Rubin-Starling (BWRS), Benedict-Webb-Rubin-Lee-Starling (BWR-LS), and a calibrated Peng-Robinson (PRC), are evaluated against experimental data for CO_2 -N_2 and CO_2 -O_2 binary mixtures. Through mean square error (MSE) analysis, the PRC EoS demonstrated the highest accuracy, especially within the relevant temperature range for CO_2 purification. However, due to PRC's computational instability in the simulation software, the more robust PR EoS was used for optimization, with final solutions validated using PRC for accuracy. Once the EoS was selected then the simulation models of the CPU were validated by comparing their outputs with published results, showing minimal deviations in mass flow and CO_2 purity, confirming their reliability.

The technoeconomic optimization was conducted using SCR, a novel derivative-free, surrogate-based global optimization algorithm developed during this PhD (Fig.1). SCR, designed for complex black-box problems with nonlinear constraints, uses Latin Hypercube Sampling (LHS), Kriging surrogate models, and CMA-ES for global optimization, with RQLIF for local refinement. The SCR algorithm was benchmarked against NOMAD, CMA-ES, and RBFOPT on both unconstrained and constrained test problems, demonstrating superior performance. Additionally, SCR, NOMAD, and RBFOPT were compared on a noisy VPSA simulation model, with SCR proving to be the most robust, especially with non-feasible starting points.

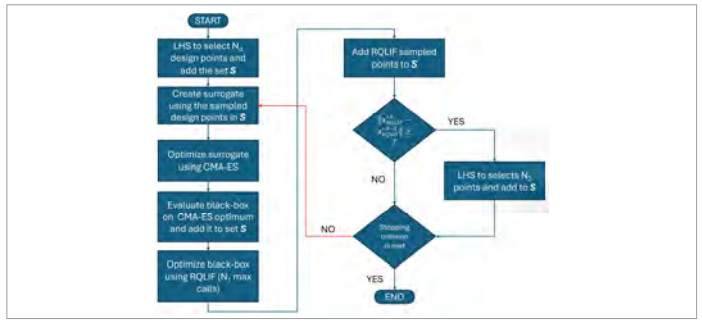

Fig.1 - Block flow diagram of SCR algorithm

The optimization of the CPUs considered CO_2 purity, CO_2 recovery, energy consumption, and capital and operating costs, using three distinct feed gas compositions: VPSA from a cement plant, membrane separation from a natural gas combined cycle, and an Allam cycle. Optimized CPUs were compared using six key performance indicators (KPIs): Specific Energy Consumption (SEC), Total Annual Cost (TAC), Specific Cost per CO_2 captured (SC), CO_2 recovery efficiency, CO_2 purity, and O2 concentration (Fig.2).

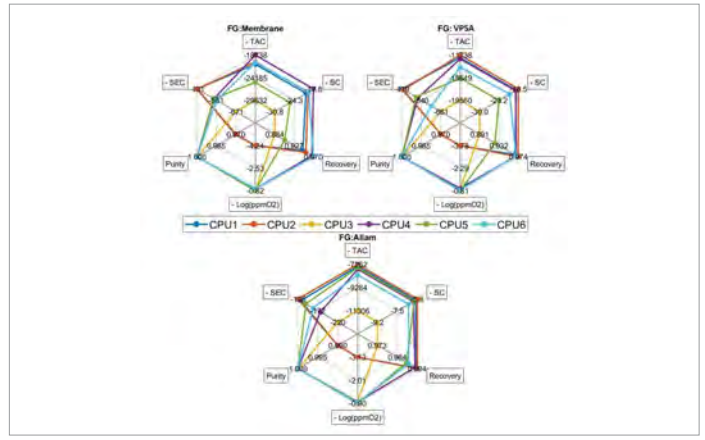

Fig.2 - Comparison of KPIs of all CPUs

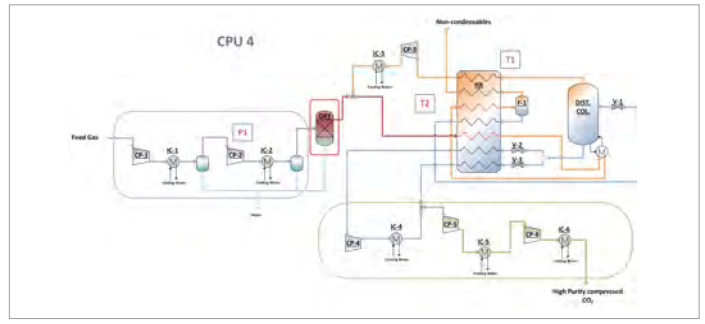

Fig.3 - Process flow diagram of CPU which provided best results

The results of six CO_2 Purification Units (CPUs) revealed significant differences in performance and cost. Flash-based CPUs struggled to meet purity requirements, particularly concerning oxygen concentration, despite having the lowest total annual cost (TAC) and specific cost (SC). Distillation-based achieved high purity but incurred the highest costs and energy consumption with the lowest recovery. Flash-distillation-based CPUs emerged as the most effective, balancing high purity (over 99.99%) and low oxygen concentration with competitive costs, often outperforming flash-based CPUs. The choice of feed gas significantly impacted CPU performance. High-purity feed gas, such as from the Allam cycle, resulted in higher recoveries and lower specific costs across all CPUs. Conversely, lower-purity feed gas from VPSA or membrane separation led to reduced recoveries and increased costs. Increasing carbon tax values generally enhanced recovery for most CPUs, though at the expense of higher specific energy consumption (SEC). Ultimately, the research concluded that combined flash and distillation-based CPUs, particularly the CPU shown in Fig.3, offer the best balance of purity, recovery, and cost-effectiveness for integrating with carbon capture systems.

INTEGRATION OF SEWGS AND DISPLACE TECHNOLOGIES IN STEEL PLANTS FOR MITIGATION OF CO_2 EMISSIONS

Nicola Zecca - Supervisor: Giampaolo Manzolini

The steel industry is a pillar of modern society, since steel products are widely used in many sectors such as construction, infrastructure, transportation, and consumer goods. However, it is also one of the most energy-intensive and carbon-emitting industries, accounting for approximately 8% of global energy demand and 7% of total emissions from the energy system. The current steelmaking processes predominantly utilize iron ore and recycled steel scrap. About 70% of the metallic input derives from iron ore, while scrap accounts for the remaining 30%. The blast furnace process, which uses iron ore as the main input, accounts for 90% of production from iron ore. Scrap-based production is carried out in electric furnaces, which are significantly less energy-intensive. The production of each tonne of steel still results in an average of 1.4 – 1.9 tonnes of CO_2 emissions. Another primary production method is the direct reduced iron-electric arc furnace (DRI-EAF) route, which differs from BF-BOF by using high-quality DRI pellets instead of raw iron ore. Reduction occurs in a solid state in a shaft furnace before melting in the EAF, often combined with scrap. This route utilizes hydrogen and carbon monoxide as reducing agents, with natural gas predominantly used to generate the required syngas.
Similarly, the fertilizer sector is responsible of a significant share of global CO_2 emissions. The global ammonia and urea sectors are critical to modern agriculture and various industrial applications, playing pivotal roles in meeting global food demands and supporting industrial processes. Ammonia, synthesized primarily through the Haber-Bosch process, combines nitrogen from the air with hydrogen derived mainly from natural gas under high pressure and temperature conditions. Ammonia is essential for producing urea, the most widely used nitrogen fertilizer. Urea contains approximately 46% nitrogen, making it one of the most concentrated nitrogen sources available to farmers. Its widespread use is attributed to its cost-effectiveness and efficiency in delivering essential nutrients to crops, significantly enhancing agricultural productivity and contributing to global food security.
In the thesis work, various options and technologies have been modelled and compared to perform a techno-economic assessment of low-carbon steel production pathways. The integration of innovative carbon capture technologies, such as DISPLACE and SEWGS, into conventional BF-BOF and NG-DRI-EAF routes has been modelled and compared to reference plants equipped with benchmark carbon capture technologies, such as MEA and MDEA scrubbing (Table 1). Additionally, CCUS pathways have been considered, analysing the benefits of industrial symbiosis between the steel and fertilizer sectors. Part of the work presented in this thesis was conducted within the context of the C⁴U and INITIATE projects. The objectives of the thesis can be summarised as follows:

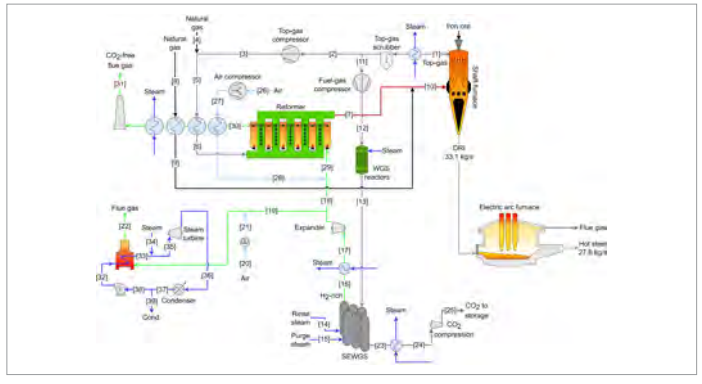

Fig.1 - Plant layout of DRI-EAF + SEWGS process.

- Development of dedicated models in Aspen Plus to implement DISPLACE and SEWGS technologies within the layout of conventional steel plants, aiming to reduce the carbon footprint of steel production (Figure 1).
- Techno-economic analysis of the C⁴U steel mill, of the INITIATE process and of the DRI-EAF steel production route with the integration of carbon capture technologies.
- Development of models in Aspen Custom Modeller to conduct dynamic simulations of the INITIATE process, capturing the time-dependent behaviour of the mass flow rate and composition of the basic oxygen furnace gas used as feedstock for ammonia production.
- Contribution to a deeper understanding of best practices for integrating SEWGS and DISPLACE carbon capture technologies within steel mill layouts.

The SEWGS technology converts syngas into streams of H_2 and CO_2, making it suitable for precombustion CO_2 capture. It operates in pressure swing adsorption mode, where the produced CO_2 is in situ adsorbed on solid materials at temperatures between 350 and 550 °C while the WGS reaction takes place. The DISPLACE technology utilizes an isobaric separation method for post-combustion CO_2 capture from flue gases. It operates on a multicolumn concentration swing principle, delivering two separate product streams. In the feed step, CO_2 is adsorbed onto a sorbent, leaving the gas stream CO_2-lean, while the sorbent is regenerated by displacing CO_2 with steam, resulting in a CO_2-rich product, without requiring pressure or temperature swings.
The techno-economic analysis of the C⁴U plant demonstrates that DISPLACE and CASOH technologies can significantly reduce emissions of a conventional BF-BOF steel mills. Detailed analyses were conducted to optimize operational conditions for DISPLACE in various units, revealing its superiority over the benchmark MEA post-combustion technology under certain CO_2 concentration thresholds. The thesis also explores the concepts of industrial symbiosis and circular economy. The INITIATE project exemplifies progress towards a sustainable future for both the steel and fertilizer sectors, particularly in the case of the large-scale INITIATE plant, which achieves substantial CO_2 emission reductions in steel and urea production. When compared to reference cases, large-scale INITIATE plant exhibits lower carbon avoidance costs under conditions of low electricity prices and high natural gas prices. However, large-scale INITIATE plant reaches higher level of carbon avoidance.
The steel sector is expected to see an increase of DRI-EAF market share in the coming decades, with H_2-DRI-EAF gaining traction. The decarbonisation of the DRI-EAF process can be attained transitioning the reducing gas fed to the shaft furnace from a syngas generated from fossil fuels to pure H_2. However, this transition presents various challenges such as ensuring the availability of green hydrogen, maintaining optimal temperatures in shaft furnaces, and addressing the absence of carbon in DRI. Given these challenges, integrating carbon capture technologies presents a promising avenue for mitigating CO_2 emissions in the DRI-EAF process, with potential for achieving up to 90% carbon avoidance when utilizing electricity generated from renewable or nuclear sources.
Interesting future work could regard exploring the feasibility of injecting the H_2 generated from SEWGS in a shaft furnace and thus coupling a BF-BOF plant with a DRI-EAF reaching in this way elevate levels of reduction of CO2 emissions.

PLANT	SIZE	TECHNOLOGY	CO_2 CAPTURE
C⁴U	9249 tHRC/day	BF-BOF	DISPLACE CASOH
INITIATE	9249 tHRC/day 224 turea/day	BF-BOF Conventional	SEWGS
	9249 tHRC/day 1500 turea/day	BF-BOF CO2 stripping	
Steel	2382 tHRC/day	DRI-EAF	SEWGS

Tab.1 - Overview of the analysed plants with innovative carbon capture technologies.

MECHANISTIC MULTI-SCALE MODELLING OF FISSION PRODUCT BEHAVIOUR IN OXIDE FUELS FOR APPLICATION TO GENERATION III AND IV NUCLEAR REACTORS

Giovanni Zullo - Supervisors: Lelio Luzzi, Davide Pizzocri

My work focuses on the development and assessment of SCIANTIX (version 2.0), an open-source meso-scale code upgraded to describe gaseous and volatile Fission Product (FP) behaviour in UO2 nuclear fuel, together with peculiar microstructural phenomena. Additionally, the work encompasses a comprehensive separate-effect validation of the physics-based models I developed/upgraded and included in the code, together with the first-of-a-kind integral validation of the code, working as a module online coupled with integral thermo-mechanical Fuel Performance Codes (FPCs), applied to both stationary and transient Light Water Reactor (LWR) fuel rod conditions. Standard methodologies for developing nuclear FPCs usually rely on empirical correlations that interpolate the fuel behaviour in specific temperature and burnup ranges, limiting their effectiveness to novel operative conditions or innovative fuel rod systems. Moreover, particular upgrades of FPCs (such as those based on data-assimilation or machine learning techniques) face the additional challenge of adapting to their pre-existing code architectures. To overcome these limitations, using mechanistic meso-scale codes demonstrated the potential for exploring new reactor conditions, fuel systems, and innovative models by leveraging the multi-scale modelling approach. None of the existing meso-scale mechanistic codes is open-source, and SCIANTIX 1.0 was developed as the first open-source engineering code for fission gas behaviour in nuclear fuel. Compared to the original version, the SCIANTIX meso-scale code (version 2.0) that I developed in this work: (I) Features an object-oriented architecture, which I adapted to model nuclear materials (e.g., through specific classes representing the behaviour of irradiated fuel and gaseous and volatile FPs). Moreover, this new object oriented architecture provides the code with the essential properties of modularity, reusability, maintainability, and flexibility, which align with the requirements of a qualifiable code. (II) Includes a set of new original physics-based models I developed describing the behaviour of radioactive gaseous and volatile FPs (with a particular focus on gaseous isotopes of radiological concern, so far considered in FPCs only through semi-empirical correlations), the formation and evolution of High-Burnup Structure (HBS) porosity (so far neglected by FPCs), and the helium behaviour (relevant for fuel storage scenarios). (III) includes an extended spectral diffusion algorithm, which I rigorously verified in stationary and transient conditions. As mentioned, the new (standalone) SCIANTIX 2.0 comes with an organised separate-effect validation database, built on publicly available experimental data, confirming the accuracy of each model I included (namely, stable and radioactive gaseous/volatile FPs, HBS porosity, and helium behaviour). In addition, I personally worked on coupling the code with several FPCs (TRANSURANUS, FRAPCON, FRAPTRAN, OFFBEAT). Through such a multi-scale approach, the last important outcome of this work is the integral validation of SCIANTIX 2.0 in LWRs fuel rod conditions. With these coupled FPCs, I simulated the behaviour of a large number of LWR rods belonging to the IFPE database in nominal and transient conditions, assessing the performance of the coupled codes in terms of significant figures of merit (e.g., integral stable/radioactive gas release, as predicted by the SCIANTIX 2.0 code)