MECHANICAL ENGINEERING | PHYSICS | PRESERVATION OF THE ARCHITECTURAL HERITAGE | SPATIAL PLANNING AND URBAN DEVELOPMENT | STRUCTURAL SEISMIC AND GEOTECHNICAL ENGINEERING | TECHNOLOGY AND DESIGN FOR ENVIRONMENT AND BUILDING | TERRITORIAL DESIGN AND GOVERNMENT | AEROSPACE ENGINEERING | ARCHITECTURAL AND URBAN DESIGN | ARCHITECTURAL COMPOSITION | ARCHITECTURE, URBAN DESIGN, CONSERVATION OF HOUSING AND LANDSCAPE | BIOENGINEERING | BUILDING ENGINEERING | DESIGN | DESIGN AND TECHNOLOGIES FOR CULTURAL HERITAGE | ELECTRICAL ENGINEERING | **ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY** | ENVIRONMENTAL AND INFRASTRUCTURES ENGINEERING | INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING | INFORMATION TECHNOLOGY | INTERIOR ARCHITECTURE AND EXHIBITION DESIGN | MANAGEMENT, ECONOMICS AND INDUSTRIAL ENGINEERING | MATERIALS ENGINEERING | MATHEMATICAL MODELS AND METHODS IN ENGINEERING

PhD Yearbook | 2016

DOCTORAL PROGRAM IN ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY

Coordinator:
Prof. Carlo Bottani

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

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

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

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY - 28TH CYCLE	
AL-DAHIDI Sameer Mahmoud Ahmed	Development of Data-Driven Methods for Prognostics and Health Management under Variable Operational Conditions in Industrial Equipment
BESAGNI Giorgio	Bubble column fluid dynamics: experimental and numerical investigations
BORTOT Davide	A novel avalanche-confinement TEPC for microdosimetry at nanometric level
DI MARCOBERARDINO Gioele	Application of gas fuels to membrane reactor for small-scale power production
GARDUMI Francesco	A multi-dimensional approach to the modelling of power plant flexibility
GEROSA Matteo	Ab Initio Studies of Bulk and Defective Oxides Using Nonempirical Hybrid Density Functionals
GUANDALINI Giulio	"Power-to-gas" and energy storage systems based on hydrogen technologies
HU Yang	Development of Prognostics and Health Management Methods for Engineering Systems Operating in Evolving Environments
LASALA Silvia	"Advanced cubic equations of state for accurate modelling of fluid mixtures. Application to CO2 capture systems"
LORENZI Stefano	Improvement of the Control-Oriented Modelling of the Gen-IV Lead-cooled Fast Reactor: Development of Reduced Order Methods
MAFFINI Alessandro	Laser cleaning of diagnostic first mirrors for nuclear fusion machines
MAZZOLINI Piero	Functional Properties Control of Doped TiO2 for Transparent Electrodes and Photoanodes
MOSSINI Eros	Novel i-SANEX/GANEX Formulation for Hydrometallurgical Actinide Separation from Spent Nuclear Fuel
NAJAFI Behzad	Predictive Modelling and Adaptive Long-term Optimization of a High Temperature PEM Fuel Cell Based Micro-CHP System
SAGIA Eleni	Silicon Microdosimetry in Hadron Therapy Fields
SASHALA NAIK Alvin	Neutron Dosimetry and Spectrometry in Complex Radiation Fields using CR-39 track detectors
SPINELLI Maurizio	Advanced Technologies For Co2 Capture And Power Generation In Cement Plants
TURI Davide Maria	High Fidelity 1d Model for Selective Membrane Simulation in Ccs Power Plants
ZANETTI Matteo	Development of new tools for the analysis and simulation of Circulating-Fuel Reactor power plants

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY - 27TH CYCLE	
SCOCCIA Rossano	Modelling and experimental evaluation of a double effect thermal driven air conditioning system using ammonia/water absorption and desiccant evaporative cooling

ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY - 26TH CYCLE	
CORRADA Paolo	Low Temperature Solar Cooling System with Absorption Chiller and Desiccant Wheel

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

STEN ADVISORY BOARD		
Surname	*First Name*	*Insitute*
Bruna	Gianni	IRSN
Lontano	Maurizio	Istituto di Fisica del Plasma - CNR
Romer	Arturo	Nuklearforum
Lombardi	Carlo	EnergyLab Foundation
Ortis	Alessandro	Fondaz. Einaudi/OPEF
Rosatelli	Franco	Chief Technological Officer – Ansaldo Energia
Muzzio	Adriano	Unione Italiana Termofluidodinamica
Pastorino	Giorgio	Peltech srl - Lecco

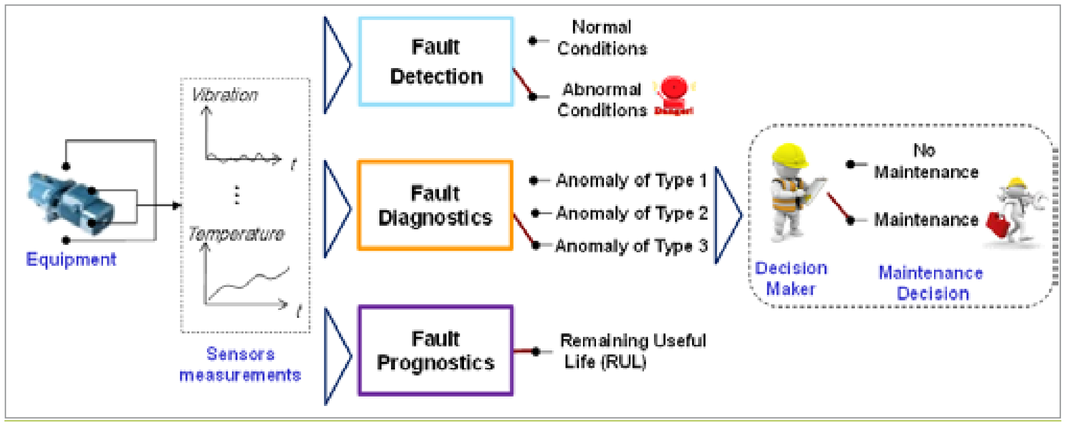
DEVELOPMENT OF DATA-DRIVEN METHODS FOR PROGNOSTICS AND HEALTH MANAGEMENT UNDER VARIABLE OPERATIONAL CONDITIONS IN INDUSTRIAL EQUIPMENT

Sameer Al-Dahidi - Supervisors: Dr. Francesco Di Maio, Prof. Enrico Zio

Co-supervisor: Prof. Piero Baraldi

Prognostics and Health Management (PHM) is a field of research and application aiming at detecting the degradation onset of industrial equipment, diagnosing its faults, predicting its failure time and proactively managing its maintenance to avoid shutdown by means of fault detection, fault diagnostics and fault prognostics systems, respectively (refer to Figure 1). PHM relies on diverse sources of information collected through sensors placed on the equipment representative of the equipment behaviour (e.g., vibration) and of the operational conditions the equipment is subjected to (e.g., temperature) that affect the equipment behaviour information.

This PhD work addresses the challenges that fault detection, fault diagnostics and fault prognostics systems development faces when dealing with industrial equipment working under variable operational conditions. In this work, novel computational methods are proposed to address the detection of incipient faults, the diagnostics of their causes and the prognostics of the available time to undertake effective countermeasures on an equipment working under variable operational conditions. Firstly, a method is proposed for quantifying and controlling the uncertainty affecting the performance of a fault detection system due to the variable operational conditions experienced by an equipment during its life, based on the offline estimation of Prediction Intervals (PIs) with a predefined confidence level by using Order Statistics (OS) theory. PIs are, then, exploited within an online non-parametric, sequential decision strategy to assess whether the equipment is working in normal or abnormal conditions irrespective of the actual operational conditions. This method will be shown to overcome traditional auto-associative approaches when dealing with fault detection under variable operational conditions, for example during transients affected by large process uncertainty.
Once an abnormal condition is detected, a fault diagnostics system is generally used to identify the causes of the occurred abnormality. This is traditionally done by partitioning the collected data into dissimilar groups (whose number is generally "a priori" unknown, that makes the problem unsupervised) and, then, among these, identifying the characteristics of the different groups of behavior. To this aim, an unsupervised ensemble clustering method is developed for identifying the characteristics of the equipment behaviour under different operational conditions that can be provided to the diagnosis system as an adjuvant information that may enhance the characterization of the causes of degradation process that leads the equipment towards failure.
Finally, the benefit of utilizing the information collected on an heterogeneous fleet of equipment experiencing different operational conditions is shown on the performances of both fault diagnostics and fault prognostics systems. With respect to the former, a framework of analysis is proposed that capitalizes all the available information of the fleet by incrementally learning different equipment behaviours and operational conditions of the fleet, without forgetting the previously learnt knowledge. With respect to the latter, a method based on an Homogeneous Discrete-Time Finite-State Semi-Markov Model is proposed to model the degradation process and, correspondingly, estimating the Remaining Useful Life (RUL) of an equipment of a fleet, whose operational conditions are fundamental to characterize the states describing the process.
The effectiveness of the proposed fault detection approach is demonstrated on real industrial case concerning 27 shut-down transients of a Nuclear Power Plant (NPP) turbine, whereas the proposed fault diagnostics approaches are applied to a fleet of two NPPs turbines of 149 and 116 shut-down transients. Finally, the applicability of the proposed fault prognostics approach is shown on two case studies regarding an heterogeneous fleet of aluminum electrolytic capacitors used in electrical automotive industry and an heterogeneous fleet of turbofan engines used in aircraft industry. Results show that, in case of industrial equipment working under variable operational conditions, the proposed PHM methods allow obtaining more accurate, robust and precise detection, diagnostics and prognostics results than with traditional PHM approaches.



1. PHM systems.

BUBBLE COLUMN FLUID DYNAMICS: EXPERIMENTAL AND NUMERICAL INVESTIGATIONS

Giorgio Besagni - Tutor and Advisor: Prof. Fabio Inzoli

Bubble columns are multiphase reactors where a gas phase is dispersed into a continuous phase (liquid phase or a suspension) by means of a sparger. They can be designed to work either in semi-batch mode or in continuous mode (with the continuous phase moving with or counter the dispersed phase). In this dissertation we focus on gas-liquid bubble columns, which are widely used in the chemical, petrochemical and biochemical industries because of a number of advantages they provide both in design and operation (i.e., excellent heat and mass transfer, and low maintenance due to lack of moving parts). However, the interactions between the phases inside the reactor are extremely complex, making their design and scale-up very difficult. Moreover, in most industrial applications, internal devices are added to control heat transfer, to foster bubble break-up or to limit the liquid phase back-mixing. These elements can have significant effects on the multiphase flow inside the bubble column reactor and the prediction of these effects is still hardly possible without experimentation. There is a large amount of research ongoing for understanding the fluid dynamics and the transport phenomena involved to support the design and scale-up methods. In this respect, four scales need to be considered: the molecular scale, the bubble scale, the laboratory-reactor scale and the industrial scale. At the molecular scale, fundamental chemistry is used to study and model the heat and mass transport phenomena at the interface. At the bubble scale, investigators study bubble shapes, size distributions, the bubble motion, and the coalescence and break-up phenomena. At the laboratory-reactor scale, the focus is given to the global fluid dynamics (i.e., the holdup, the holdup radial distribution, and the gas and liquids phase motion) and to the flow regime transitions. Finally, scale-up models are applied to predict the performance at the industrial scale (high pressure and temperature). In spite of the industrial interest, there is a lack of studies considering the influence of the counter-current operation mode, the column design (i.e. the presence of internals) and the liquid phase properties in large-diameter bubble columns. In addition, the data, the correlations and the regime transition criteria obtained in small-diameter columns cannot be used to understand the fluid dynamic in large-diameter ones. Therefore, ad-hoc experimental investigations and numerical models should be provided for supporting the reactor design and scale-up. This dissertation contributes to the existing discussion by studying, experimentally and numerically, a large-diameter bubble column. The experimental investigation was conducted on an ad-hoc large-diameter (and large-scale) bubble column. The column - 0.24 m inner diameter and 5.3 m height – was tested in the annular gap and in two open tube (pipe sparger and spider sparger) configurations. In the annular gap configuration, the air was introduced up to a superficial gas velocity of 0.23 m/s and the water was recirculated up to -0.11 m/s. In the open tube configurations, the air was introduced up to a superficial gas velocity of 0.20 m/s and the water was recirculated up to -0.09 m/s. Furthermore, the spider sparger bubble column was tested using various liquids and aqueous solutions of electrolytes to study the effect of the physical properties of the liquid phase. The liquid phases tested were: pure water, water with NaCl, mixture of water-ethanol and mixtures of water-monoethylene glycol. We coupled different experimental techniques to provide a comprehensive view of the bubble column fluid dynamics, considering both the bubble and the laboratory-reactor scales. To this end, holdup, gas disengagement, image analysis and optical probe measurements were used to investigate the relations between the global column fluid dynamics, the flow regime transitions, the bubble shapes and size distributions, and local flow properties. The holdup measurements are compared with the literature and are used to investigate the flow regime transition. The gas disengagement measurements are used to further investigate the flow regime transition and study the structure of the holdup curve. The image analysis is used to study the bubble shapes and size distributions near the sparger and in the developed region of the column; in particular, the image analysis is applied to different gas velocities in the homogeneous regime in both the batch and counter-current modes. The optical probe is used to acquire radial profiles of the local properties (i.e., local void fraction and bubble rise velocity) to study the flow properties and further investigate the flow regime transition. In addition, a correlation between bubble shape and size is obtained and is implemented in an algorithm for the conversion of bubble chord into diameter distributions. Comparing the results from the different techniques, the influence of the different parameters (i.e., liquid superficial velocity, gas superficial velocity, liquid phase properties, presence of internals and sparger design) is discussed considering all main aspects of the two-phase flow, from the local flow properties to the global flow features. The presence of the internals and the sparger design have a limited influence on the global fluid dynamics, probably because of the large-diameter of the bubble column and the large sparger openings. The counter-current mode is found to increase the holdup, reduce the bubble rise velocity, destabilize the homogeneous regime and change the local flow properties. Finally, the changes in the liquid phase mainly influence the bubble properties, thus resulting in a change of the bubble size distribution, and, therefore, affecting the regime transition and the holdup curves. In particular, we observed a relation between the bubble scale and the global fluid dynamics (laboratory-reactor scale): small (large) bubbles stabilize (destabilize) the homogenous regime and increase (decrease) the holdup. The above-mentioned relationship between the bubble scale and the global fluid dynamics (laboratory-reactor scale) may be governed, mainly, by the lift force. In particular, the lift force induces the changes in the bubble size distributions and affects the motion of the small and large bubbles. In this respect, the lift force affects the bubble column fluid dynamics and the regime transition.

In the numerical part, a Population Balance Model and a Computational Fluid Dynamics (CFD) model are proposed. The Population Balance Model is able to predict the bubble size distributions in the developed region of the bubble column. The CFD model, based on a bi-dispersed Eulerian approach, provides an insight into the column two-phase flow. The CFD model is able to reproduce the homogenous regime of the annular gap bubble column, but performs poorly with the spider sparger bubble column. However, the performances of our approach – for the spider sparger bubble column – are comparable with the ones of the state-of-the-art HZDR Baseline model in its fixed polydispersity formulation. Therefore, the proposed approach is a promising method for the simulation of large scale bubble columns.

In conclusion, this research enhances the knowledge of bubble column fluid dynamics, provides a large and comprehensive dataset for model validations and offers modeling approaches to improve the design and scale-up of multiphase reactors.

A NOVEL AVALANCHE-CONFINEMENT TEPC FOR MICRODOSIMETRY AT NANOMETRIC LEVEL

Davide Bortot - Supervisor: Prof. Andrea Pola
Tutor: Prof. Stefano Agosteo

Microdosimetry and track-nanodosimetry belong to a branch of the radiation physics which concerns the study of theoretical and experimental methodologies able to perform a detailed analysis of the radiation interaction with matter, in particular with biological tissue at cellular and sub-cellular level. This kind of analysis has a direct impact in the hadron therapy field, an emerging radiotherapeutic treatment carried out with hadrons (protons and other ions such as carbon ions), which constitutes a promising solution for certain radioresistant cancers and for cancerous tumors close to critical organs. The assessment of the biological effective dose of clinical hadron beams is based on the measurements of the absorbed dose, which is a macroscopic and averaged quantity that demonstrated to be not adequate to describe the energy deposition process at micrometric level, because it does not take into account neither the stochastics of particle interaction in the target volume nor the track structure of ionizing charged particles, which is decisive for the initiation of the radiation damage. A more comprehensive physical knowledge of the local energy deposition can be accomplished with high accuracy by innovative methodologies and instruments provided by microdosimetry, which aims at characterizing the statistical fluctuations of the local energy imparted at the micrometric level, and track-nanodosimetry, devoted to the description of the pattern of particle interactions at the nanometric level.
To date, the Tissue Equivalent Proportional Counter (TEPC) is the most accurate device to measure the microdosimetric properties of a particle beam, showing to properly assess the relative biological effectiveness by linking the physical parameters of the radiation with the corresponding biological response. Nevertheless, at present it is not possible to characterize a particle beam by using the only microdosimetric distributions since empirical weighting functions are still necessary. The motivation arises from the fact that the biological damage induced by radiation starts with injuries to sub-cellular structures, such as the chromatin fibers and the DNA segments, therefore the cell damage is strictly related to the spatial distribution of the interaction points between the charged particle and matter. This track structure plays a significant role at the nanometer level, where the site size is smaller than the ion track structure.
The microdosimetric approach is not able to provide detailed information about that, since it is based on the local energy imparted to sensitive volumes of matter at micrometer length scale. Common TEPCs, in fact, are able to measure single event spectra in micrometric sites, down to about 0.3 µm. On the other hand, the pattern of particle interactions at the nanometer level is measured by track-nanodosimeters, which derive the single-event distribution of ionization cluster size for sites of a few nanometers up to 20 nm. Nanodosimetric quantities demonstrated to have a strong correlation with radiation-induced damages to the DNA. Nevertheless, from a practical point of view, all the present nanodosimeters (only three different prototypes worldwide) show really huge limitations, which are due to their complexity and dimension. A great challenge in this sense would be to design and built a portable instrument able to fill the gap between common TEPCs and nanodosimeters and practically useful for track measurements in different therapeutic beams.
For all these reasons, this doctoral research project aimed at studying the feasibility of extending the performances of standard tissue equivalent proportional counter down to the nanometric region.
By exploiting a preliminary work presented in literature, an extensive study of a new TEPC able to measure microdosimetric distributions in simulated biological sites from 0.3 µm down to 25 nm in diameter was performed. This innovative TEPC, able to confine the electronic avalanche inside a defined volume, was designed and constructed together with a customized and transportable vacuum and gas flow system. The peculiarities of the new design are mainly a thin wall chamber, which allows the microdosimeter to measure with hadron beams, and the presence of a removable but internal alpha source and a very compact Solid State Detector for test and energy calibration purposes. The dimensions of the entire system were minimized to make it easily transportable and versatile, with the aim at performing measurement campaigns at different facilities.
The first phase of the characterization activity was devoted to the study of the optimum operating conditions of the detection system by determining the proper bias voltage and pressure combinations, the stability and the performances of the whole apparatus. This was accomplished through the determination of the so-called "electron transmission windows", empirical charts reporting the best operating conditions of the device in terms of polarization of the three electrodes at a selected simulated site size. A procedure for the calibration of the microdosimetric spectra based on the internal alpha source was also setting up and exploited.
The response of the device to photons emitted by a Cs-137 isotopic source and to fast neutrons was characterized experimentally at different simulated site sizes and configurations. The analysis of the microdosimetric spectra demonstrated the good performances of the device and the reproducibility of the calibration procedure.
Since the main objective of this doctoral project concerned the feasibility study of a new type of TEPC which could fill the actual scientific gap between the approaches proposed by experimental microdosimetry and track-nanodosimetry for the physical characterization of hadron beams, the response of this novel avalanche-confinement TEPC to a low-energy carbon ion beam was experimentally evaluated. Several configurations were tested by changing both the simulated site size from 0.3 µm down to 25 nm and the depth along the Bragg peak of the dose distribution of the delivered beam. This irradiation campaign gave confidence about the capability of this novel avalanche-confinement TEPC of measuring in the range 0.3 µm - 25 nm when irradiated with low-energy carbon ions. It should be underlined that microdosimetric measurements of hadron beams at the nanometric scale with portable devices have never been performed before.
The knowledge and the results acquired during this doctoral project will be exploited for designing and developing a new facility constituted by a track-nanodosimeter coupled with a wall-less avalanche-confinement TEPC, with the purpose of directly correlating the microdosimetric spectra with the track-nanodosimetric distributions at the same experimental conditions. The microdosimetric spectra measured by such a device consist in the convolution of core and penumbra events, the two components of a particle track measured through a nanodosimeter. A systematic comparison between the microdosimetric and track-nanodosimetric distributions for the same particle beam will allow to investigate the possibility of unfolding the microdosimetric spectrum into its different track components and any limits of this technique. In such a way, the beam characteristics measured by a portable TEPC could be transferred to a track-nanodosimetric description, much more relevant in the framework of the biological damages to the nanometric targets, such as the DNA and the chromatin fiber.

LOW TEMPERATURE SOLAR COOLING SYSTEM WITH ABSORPTION CHILLER AND DESICCANT WHEEL

Paolo Corrada - Supervisor: Prof. Cesare Maria Joppolo

By 2008, a total of approximately 450 solar cooling systems were realized worldwide. Approximately 60% of these systems use absorption chillers, 11% adsorption chillers and 29% open systems (desiccant evaporative cooling and liquid sorption systems). Even so, the total volume of installations reveals that the solar cooling sector is still a niche market. This is mainly due to the fact that solar cooling systems require high upfront installation costs due to the costly high-grade solar collectors and the cost of an absorption chiller.

Absorption chiller

Absorption systems are similar to vapour-compression air conditioning systems but differ in the pressurisation stages. They are heat-operated devices that produce chilled water without the use of a compressor via an absorption cycle allowing a significant reduction in the electricity consumption. One of the heat source can be hot water that in the case of a solar cooling system is obtained by the use of solar panels.
As in the vapour compression, in the absorption refrigeration cycles the removal of heat is achieved through the evaporation of a refrigerant at a low pressure and the rejection of heat through the condensation of the refrigerant at a higher pressure. The addition of heat in the generator is used to separate the low-boiling refrigerant from the solution.

Desiccant wheel

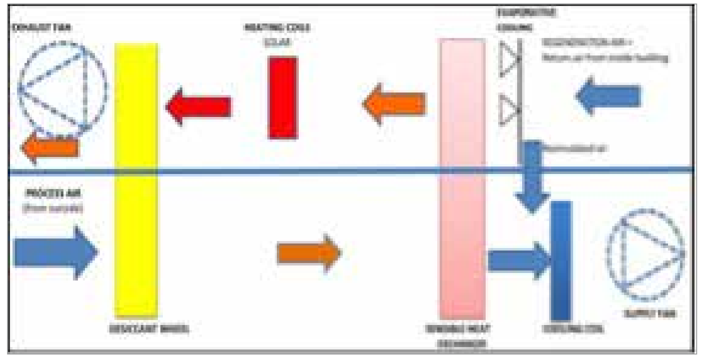
A way to remove the humidity from an air stream is by using a rotary wheel impregnated with a hygroscopic material. Rotary wheels are operated within two separated sections, namely the adsorbing section where dehumidification occurs, and a regeneration section (desorption of water vapour) where the desiccant is reactivated by passing hot air. The regeneration and adsorption air streams are in a counter flow arrangement.
When exposed to low relative humidity, desiccant materials come to equilibrium at low moisture contents, and conversely exposure to high relative humidity results in equilibrium at high moisture contents. After the desiccant adsorbs the moisture, it becomes wet and hot (exothermic reaction) and its surface vapour pressure becomes high. When the level of humidity in the air stream falls below the saturation point of the desiccant, it will begin to release moisture back into the air stream.

Methodology

The design of the suggested system is based on a pure theoretical model. The model includes several parts, which are then integrated to develop a final model of an Air Handling Unit (AHU) which include a desiccant wheel. Thermodynamical modelling of the single components starts from basics assumptions and provides as output the properties of each component. In particular the following mathematical models have been developed with the Matlab™ software for the estimation of energy output from a solar field, the absorption chiller, the desiccant wheel and an AHU. These four models have been integrated to generate a solar cooling system implementing absorption and adsorption technologies and compare its efficiency with the efficiency of a traditional solar cooling system implementing only absorption technology.
A specific methodology has been conceived in order to separate and clearly accomplish the various tasks. The developed models have been validated by using data available in literature.

New system design

In a HVAC system, dehumidification of the air is usually achieved in the AHU where air flows through a cooling coil; air is cooled until its dew point and water vapour is condensed.
Dry air is then heated through a second coil to the desired supply temperature. This design of the AHU integrated in a solar cooling system is the most diffused and it is the reference one.
The main difference in the proposed system is the integration of a desiccant wheel and of a sensible heat exchanger in the AHU. Also the heating coil before the supply fan has been removed, as for the way humidity is removed, the treated air in this system does not need to be re-heated.
Two air streams are necessary in this configuration: the process air flow, which is the air flow treated in order to balance the ambient latent and sensible loads and the regeneration one which is necessary to remove water vapour from the desiccant wheel matrix. Cooling coil, heating coil and fans are the same of the reference design. The heating coil on the regeneration side is fed directly by dedicated solar thermal panels.
The outside air passes through a desiccant wheel and becomes warmer and drier. The air then flows through a sensible heat exchanger and the temperature is reduced. The dry, cooled air is then mixed with the return air from the conditioned areas before it passes through a cooling coil where the air is further cooled to the required temperature before being supplied to the user. By removing the humidity of the outside air using a desiccant wheel the cooling load on the chiller is reduced and accordingly the size of the chiller can be reduced as well as its consumption.
On the regeneration side, the regeneration air from inside the conditioned areas is cooled by an evaporating cooler unit before it enters the sensible heat exchanger where it is heated by the heat absorbed by the process air. The regeneration air passes then through the water to air heating coils to heat the regeneration air to the required regeneration temperature. The hot air then passes through the desiccant wheel at the regeneration side and exhausted to the surrounding.



1. Schematic diagram of the proposed system

Results

The performance of the system is measured in terms of the energy saving at solar field side when the proposed solar cooling system is compared to a conventional solar cooling system.
It has been found that the implementation of a desiccant wheel in a typical solar cooling system used in conjunction with an absorption chiller results in significant energy and implementation cost savings which can achieve a saving up to 56% in thermal energy.
Accordingly this saving can be translated in financial saving due to the reduced number of solar thermal panels required.
Other saving in installation cost is due to the reduced size of the absorption chiller needed.
The total energy savings achievable by implementing the proposed system vary depending on the application and the working conditions of the system.

APPLICATION OF GAS FUELS TO MEMBRANE REACTOR FOR SMALL-SCALE POWER PRODUCTION

Gioele Di Marcoberardino - Tutor: Prof. Stefano Campanari
Advisor: Prof. Giampaolo Manzolini

In the last decades, the growing electricity and heat demand leads to an intensification of the fossil fuel usage, especially for residential applications. One of the cheapest and interesting options to increase energy efficiency in this sector is the micro combined heat and power (micro-CHP) generation, where the simultaneous production and utilization of heat and power, allows for a better fuel exploitation compared to conventional power production systems. Stationary PEM fuel cells based systems offer a clean and efficient source of electricity with the highest primary energy saving potential at micro-cogeneration scale. The PhD project investigated the integration of an ATR membrane reformer within a micro-CHP system of 5 kWel and 6.5 kWth based on PEM fuel cell. The optimization of the micro-CHP system was performed, within ReforCELL and FERRET European projects, aiming at the target of 40% of net electric efficiency and 90% of total system efficiency comparing different configurations and operating conditions.
PEM fuel cells are characterized by low operating temperatures and high power density but they require ultra-pure hydrogen as fuel (CO below 10 ppm). Hence, the PhD work was focused on the development and integration of an efficient fuel processor for hydrogen production for small-scale power production. Membrane reactors, combining production and separation in one vessel, were chosen as promising technology since recent studies showed that their performances are better than conventional fuel processors.
As reference fuel, natural gas (NG) was selected since it is the most widespread distributed fuel in industrialized countries. Whereas NG composition varies significantly from country to country, the PhD purpose was to develop a mCHP-system capable of working with any NG qualities. The final version of the micro-CHP system was defined at steady state conditions and the influence of the European natural gas on the system performances had been investigated even at partial load. Finally, an analysis of dynamic behavior of the micro-CHP system was assessed to define a good control strategy when power production has to follow the quick electric energy load variation typical of small scale end-users.

Design of micro-CHP PEMFC based system at steady-state condition

A technical analysis of the micro-CHP system at rated power was developed in Aspen Plus. Different hydrogen permeate side options, vacuum pump or sweep gas, were compared together with different combination of feed temperature and pressures. A 1D two-phase phenomenological FBMR model was also used to compare and validate the quasi-lumped membrane reactor model developed for the micro-CHP system simulation in Aspen Plus. The phenomenological model was used to integrate reactor performances carried out from the experimental campaigns. The 1D model had highlighted the influence of some reactor design parameters such as u/u_{mf} and bubble size (average and maximum diameter) on the hydrogen flow rate extracted from the membrane. Regarding the overall m-CHP system, results in terms of electric efficiency and membrane area were obtained for different feed pressures (from 6 to 14 bar) and temperatures (from 550°C to 600°C). Working at lower pressure can increase electric efficiency, however it requires more membrane area increasing the leakage risks. Operating temperature seemed to be the most critical parameter: reducing the temperature from 600°C would heavily increase the membrane surface area. A good compromise between efficiency and membrane area occurred at 8 bar; S/C 2.5; 600 °C for the sweep gas case. The results for the vacuum pump showed that, despite negatively effects on the electrical efficiency of the system, some advantages could be obtained mainly from the simpler configuration of the reactor. A sensitivity analysis highlighted the influence of the main parameters and the design criteria for the definition of the CHP system.

Micro-CHP performances under different NG qualities

Power plant flexibility is fundamental to reduce production costs which is, today, one of the main weaknesses of the considered system.
The defined micro-CHP layout was used to evaluate system performances for four different natural gas compositions (Italy, The Netherland, United Kingdom and Spain). The four NG compositions, selected within the FERRET project, reflect a pure methane NG (IT), high inert concentration (NL), high ethane and propane concentrations (ES) and an average case (UK). Results showed that the Dutch NG has to be adopted as reference for the layout definition to keep the net electric efficiency above 40%. This is because the high inert content of the Dutch natural gas penalizes the hydrogen permeation driving force requiring more stringent reactor operating conditions.
In particular, the net electric efficiency of the sweep case ranges from 41.2 % with the Dutch NG to 41.6 % with the Spanish ones. The vacuum pump configuration reduces the membrane surface area by 40% but is penalized from efficiency point view achieving 39.4 % with the Dutch NG to 40.0 % with the Spanish ones. CHP simulations are also carried out at partial load: results show that the electric efficiency increases until 60-70 % of the load, then quickly drops. The micro-CHP characteristic curve is used as an input for the annual economic evaluation.

Dynamic analysis of the micro-CHP

The dynamic behavior of the micro-CHP PEMFC based system were analyzed when power production has to follow the quick electric energy load variation typical of small scale end-users. Main attention was devoted on the optimization of control strategies based on technical parameters and through a sensitivity analysis of the overall plant. The model was developed in Aspen Plus Dynamics. The modeling approach was a compromise between the computational speed and the amount of system variables. The layout was therefore characterized by some simplifications compared to the steady-state analysis.
The different components were implemented as 0D model where the output variables depend on internal correlations and by the boundary conditions.
The mass and energy balances of each component consider: accumulation phenomena, convective transport, heat transfer and chemical reactions.
Membrane reactor model consists of 3 stages where the hydrogen separation depends on the reactor temperature, feed flow and permeate side pressure. A buffer volume was placed between the reactor and the stack in order to reduce the pressure fluctuations at partial load. Regarding the HXs, a 1D finite volumes mathematical model was adopted and divided in 4 zones (from the outer to the inner): the shell (external insulated), the hot section, the tube between the flow and the cold section. The primary objective of the dynamic control was to bring the system back to a steady state condition following a quickly electric energy load variation. Results showed that although the controlled variables took several minutes to return to the set point, they always remained within the designed limits. The implemented control system, using the logic of PI and feed forward, satisfied the simulations of typical residential load profiles: the values of thermal and electrical efficiency were good in all conditions.

A MULTI-DIMENSIONAL APPROACH TO THE MODELLING OF POWER PLANT FLEXIBILITY

Francesco Gardumi - Supervisor: prof. Emanuela Colombo

Tutor: prof. Fabio Inzoli

In light of the challenges of a fast developing world and an increasing need for energy, the energy supply system of the European Union suffers from structural weaknesses. To address them, the European Commission issued long-term strategies pointing to achieve higher levels of sustainability, security and competitiveness by reducing the reliance on fossil fuels and increasing the penetration of renewable sources.

A number of mathematical models have been designed, to turn these generic indications into a more concrete energy technology and generation mix. They all seek for the mix which complies with the decarbonisation objectives set by the European Commission and guarantees the system's adequacy at the minimum global cost. All of them tend to agree over one point: the future energy system, and particularly the electricity grid, will have to become more flexible.

At present, the flexibility of the energy system relies almost only on fast ramping fossil-fuel fired power plants. In order to balance the fluctuations of renewables, these are gradually shifting their operation profiles from base- to peak-load.

The shift brings about a set of new problems and a chain reaction in the electricity supply system: power plant cycling has a cost; this causes the price bids of the companies on the market to increase and their share and revenues to decrease; this, in turn, may cause a number of companies to decommission or relocate several power plants at the same time, thus undermining the adequacy of the system. The models employed to predict the optimal long-term energy technology and generation mix do not take into account these dynamics of flexibility. Consequently, there is a risk the policies of the European Union aimed at pursuing this mix will be ineffective. The research of the author had an overall objective to address this risk and this doctoral dissertation describes how such objective was pursued.

The first part of the dissertation briefly discusses how the need for flexible energy and electricity systems arose from the new paradigm of sustainable energy supply and it states the overall objectives of the PhD research.

The second part looks into the issue of power plant flexibility and synthesizes its main features. The author analyses how the need for flexible operation of fossil-fuel fired power plants arises, stemming from the European and national long-term strategies. Thereafter, the implications of power plant flexibility on the energy supply are described. It emerges there are implications on three scales: the power plant, the electricity market and the whole energy system. At each one of these scales the requirement for flexible electricity supply causes costs and reactions of the actors to reduce these costs.

At the power plant scale, the operators experience higher costs for components wear and decreased efficiency. Their decisions to lower these costs involve power plant modifications, actions on the control systems and new O&M practices.

At the electricity market scale, the companies see the costs of the power plants increase, and they are forced into making higher bids. This reduces their market share and, therefore, their revenues. The decisions to regain competitiveness range from decommissioning or relocating capacity to trying new opportunities for revenues, such as the reserve capacity markets.

At the energy system scale, the costs arise when the dynamics related to flexibility are not taken into account and the energy mix ends up different from what envisaged by the planners. The decisions at this scale consist in anticipating the costs and reactions to flexibility at a power plant and electricity market scale, and update the forecasts and pathways to decarbonisation.

The three scales are related to one another and they involve dynamic interactions between power plant operators, companies and energy system planners. In order for these dynamics to be fully captured, an interdisciplinary research had to be carried out. It ranged from Thermodynamics and power plant Engineering, to Decision Support and Macroeconomics.

In the third part of the dissertation, the weaknesses of the models for long-term energy system planning are discussed and addressed.

The costs of flexibility and the reactions of the operators at a power plant scale are represented through two kinds of models: a thermodynamic model of a fossil-fuel fired power plant, set up with the help of Thermoflex simulation environment, and an analytical formulation of global performance indices, embeddable in electricity market and energy system models.

The thermodynamic model consists in a quasi-stationary off-design model, featuring all the relevant control logics employed in real operation. It was set up in collaboration with the operators of a power plant in the North of Italy. Its purpose is to provide the operators with an interface for predicting the thermodynamic costs of flexibility and evaluating feasible solutions for increasing the ramping capability. In line with such objective, the output of the model is indices about the off-design performance of the power plant and of the individual components, through First and Second Law of Thermodynamics quantities, respectively. The power plant model is applied to an industrially relevant case study, which is the detailed off-design performance prediction of the whole cycle and the individual components of a CCGT operating in the North of Italy, as a function of different control logics. This allowed the operators to evaluate new strategies for enhancing the cycling capability of the power plant.

The analytical formulation consists in equations for computing aggregate performance indices of the power plant in flexible operation. Specifically, the cost of the starts, the fuel cost for decreased efficiency at partial load and the cycling capability as a function of the power plant configuration are modelled.

These equations provide the link between the power plant scale and the electricity market or energy system scales: when embedded into electricity market or energy system planning models, they allow the global thermodynamic costs computed with power plant models to be fed into the electricity market or energy system models.

The costs of flexibility and the reactions of the companies at the electricity market scale are represented through a model based on Game Theory, called Stackelberg stochastic game. It is a nonlinear two-level optimisation program, which is reduced, thanks to the duality theory, to a one-level mixed-integer linear program. In addition to traditional generation dispatch models, it endogenously computes the quantity and price bids and the generation expansion strategies which guarantee each company the maximum profit, given the decisions of the other companies.

Finally, the cost of flexibility at an energy system scale is computed by modifying an existing open source energy system planning model, OSeMOSYS. The mathematical formulation derived for the cost of the starts, the costs for decreased efficiency and the cycling capability at a power plant scale is introduced into the model with proper adaptations. As other energy system models, OSeMOSYS computes the least cost long-term energy technology and generation mix, subject to constraints dictated by the European decarbonisation objectives. In addition, the introduced modifications allow the costs and dynamics of flexibility to be accounted.

The modified energy system model is applied to a test case study and to a real case study. The test case study proves that the impact of power plant flexibility on the energy system planning can be relevant; the real case study, the long-term energy planning of Cyprus, provides a small scale example of how flexibility may impact a larger system like Europe.

AB INITIO STUDIES OF BULK AND DEFECTIVE OXIDES USING NONEMPIRICAL HYBRID DENSITY FUNCTIONALS

Matteo Gerosa

Supervisors: Prof. Carlo Bottani, Prof. Giovanni Onida, Prof. Gianfranco Pacchioni

Metal oxides have been proposed as candidate materials for a number of renewable energy technologies, ranging from catalysis, to photocatalysis and solar cells. In applications involving the conversion of solar energy into chemical or electrical energy (e.g., in the case of photoelectrochemical devices or solar cells), a thorough understanding of the electronic structure and electronic excitation mechanisms is necessary. In catalytic applications instead, the chemical reactivity of the material, as well as the energetics relative to catalytic processes in which the material is actively involved, should be adequately characterized. Great challenges are posed to theory when these materials properties are to be computed using first-principles methods, with particular regard to density-functional theory (DFT) and many-body perturbation theory (MBPT). In this thesis, DFT with hybrid exchange-correlation (xc) functionals are employed for calculation of the electronic structure and ground-state properties of wide-gap oxide materials. The employed hybrid functional can be considered as nonempirical, as the fraction of exact exchange to be admixed in the xc potential is evaluated from first principles for each material using a procedure which can be rigorously justified within MBPT. Results of various benchmarks of the method are reported for both bulk pristine and defective oxides. For the latter case, oxygen vacancies are investigated as a prototypical intrinsic point defect in transition metal oxides: the calculated properties are critically compared with various experiments characterizing charge localization and excitation mechanisms in the defective material. Furthermore, aluminum-doped silicon dioxide is studied as a well-known system in which popular hybrid functional approximations fail in reproducing well-established experimental findings, due to inaccurate description of the ground state, which can be ultimately traced to the arbitrariness of the amount of exact exchange built in these functionals.

"POWER-TO-GAS" AND ENERGY STORAGE SYSTEMS BASED ON HYDROGEN TECHNOLOGIES

Giulio Guandalini - Supervisor: Prof. Stefano Campanari

Introduction

Interest in hydrogen production from electricity and water is currently increasing, discussed under the overall concept of "Power-to-gas" (P2G). In most industrialized countries, the energy system is currently changing significantly due to the massive integration of renewable energies (RES) and electric grids experience the first issues in harnessing production variability. In this scenario of growing interest for electric and chemical energy storage, finds a place the option of hydrogen production from excess or unbalancing electricity from undispatchable RES as a long-term storage or as an alternative "green" fuels source for industry or mobility. It can recover up large amounts of excess energy or stabilize the grid providing balancing services to grid operators. While direct reconversion to electricity ("Power-to-power") was the most studied options in last years, injection in the natural gas infrastructure as intermediate step for technology deployment is a fairly recent concept on which this thesis is focused. It can also contribute to decarbonization objectives in thermal sector, where electrification is not viable, together with biofuels and biogas. The long-term scenarios for P2G are focused on hydrogen mobility, as competitor of electric mobility, which portend higher revenues and markets. The analysis of this storage option is performed from different points of view and at different scales in order to check feasibility, energy efficiency and economics.

System analysis

The first section of this work is aimed at global evaluation of the system according to different timeframes and boundary conditions. Many assessments of P2G potential were recently performed for many European countries, but Italy is still missing. Long-term excess energy recovery potential is calculated according to foreseen RES share and load scenarios; methodology is based on historical time-series and technology scale up. Over a shorter horizon, a statistical model is developed in order to economically evaluate the optimal share of traditional technologies (i.e. gas turbines) and P2G capacity in order to reduce uncertainty in grid management due to wind power fluctuations. From a different point of view, the possibility for a wind park to optimize its operating strategy under technical constraints and market rules is investigated through a mixed integer linear programming model.

Electrolysis modeling

This section of the work aims at checking the influence of dynamics on the performances of the system, considering that it is not designed to work at nominal power but connected to fluctuating power source (i.e. wind turbines). This aspect is usually neglected in system analyses, but it has a relevant impact because of the connection with a fluctuating energy source (i.e. wind). The electrolysis system is modeled in Aspen Dynamics environment, considering main auxiliaries (pumps, cooling system, gas-liquid separators) and basic control strategies. A custom model for electrolysis stacks includes electrochemical behavior as function of temperature and other parameters (i.e. geometries, concentrations). Start-up, pressurization, shutdown and inertization steps are the focus of the analysis, as far as the efficiency at partial load.

Natural gas grid modeling

As mentioned before, the option of hydrogen injection in natural gas infrastructure is addressed in this thesis. Technical restrictions for this concept are currently under investigation; main issues are the maximum fraction allowed for unconventional species (i.e. hydrogen) and the impact of the continuous variability of gas composition that should be faced by final users control system. The problem of dynamics of natural gas pipelines was largely addressed in the past and much effort is still ongoing to improve algorithms performances and optimization, but they were developed for infrastructure design or optimization of operation without particular interest for different gas compositions. Nowadays, several kind of gases started to be contemporary present in the pipelines because of variety of supply, LNG terminals or biomethane injection, justifying a dynamic model with a particular focus on gas quality tracking. The model is based on spatial discretization of PDEs for compressible gas flow in pipes considering variable gas properties and "delivered energy" approach for boundary conditions. Fluctuations in properties of gas delivered to customers is than investigated in some case studies with non-conventional gas injection. In case of strong limitations, a solution could be an additional methanation step, otherwise avoided because of increased energy losses and investment costs. This solution is also interesting for CO_2 recovery and utilization for "green synthetic gas" production. Preliminary investigations are performed with Aspen Plus on traditional technology for methanation that applies the catalytic Sabatier reaction in a multi-step process. The different operating condition with respect to traditional purposes requires a specific optimization of the system. Operating conditions (temperature and pressure) and reactants flows required for "grid quality" gas production are investigated. General operation strategies (e.g. hot standby, reactants storage) are compared on economic and efficiency bases.

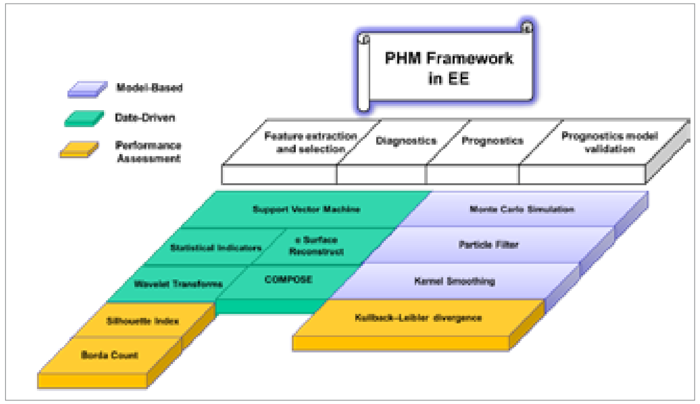
Conclusions

On long term, P2G is a viable solution for peak shaving in high-RES penetration scenarios with a relevant impact on different energy sectors (between 6-10% of current natural gas or mobility markets). With respect to long-term emissions reduction, this technology could contribute for about 4% to objectives (2050). Current curtailments or expected RES capacity on middle term horizon, are not sufficient to sustain economically P2G that remains an instrument for fluctuations balancing. Competition with traditional balancing systems is currently not economically convenient, but foreseen costs reduction and other revenue sources (unbalances compensation, ancillary services for electrical grid) lead instead to positive figures. Energy balances show a general positive recovery of wind energy, whereas from the point of view of emissions, balances are mainly neutral, or even negative, because of the additional emissions of unavoidable traditional balancing systems and reduction in electricity production. In perspective, oversized RES capacity is required to avoid this negative contribution.
The analysis of electrolysis system dynamics evidenced a relevant impact on performances, confirming the necessity to include the transient effects in global system analyses using specific models. Auxiliaries consumption and consumables (i.e. demineralized water) are not negligible and should be also considered in system analysis.
With respect to hydrogen injection in natural gas infrastructure, strongest limitation is due to the impact on gas properties regulated by grid code; consequent hydrogen fractions are low enough to not impact on operation of the system (i.e. pressure drops). Composition variations rates and ranges are generally small yielding a manageable situation for common customers. As expected, methanation yields high prices for synthetic natural gas and is convenient only in case of strong investment costs reduction and incentives for "green gas".
In this work, several aspects of P2G are investigated in order to provide a comprehensive framework of the whole supply chain. For each section, investigation methodologies are proposed and the influencing parameters evidenced. After several scenarios analyses on different scales, it can be concluded that middle- to long-term perspectives justify the effort in developing this technology in the near future.

DEVELOPMENT OF PROGNOSTICS AND HEALTH MANAGEMENT METHODS FOR ENGINEERING SYSTEMS OPERATING IN EVOLVING ENVIRONMENTS

Yang Hu - Supervisors: Piero Baraldi, Enrico Zio

Prognostics and Health Management (PHM) is a field of research and application aiming at detecting the degradation of engineering components, diagnosing the type of faults, predicting the failure time and proactively managing their failures. This PhD work addresses the problem of PHM in an Evolving Environment (EE) characterized by continuous or periodic modifications of the working conditions. The main difficulty in this context is that the information used to develop the PHM model are usually collected in a limited set of working conditions, not sufficiently representing all the possible conditions that may be experienced by the components during their lives. Thus, the general objective of this thesis is to develop an integrated framework for PHM in EE, which is capable of 1) extracting and selecting the features to be used by the PHM models; 2) detecting the occurrence of modifications (drifts) in the working conditions, and, then, adapting the PHM models to the EE; 3) assessing the performance of the developed PHM models in EE.
The feature extraction and selection problem has been addressed by developing a novel semi-supervised approach whose originality is the combined use of both labeled and unlabeled data. Labeled data containing historical examples of signal values and the corresponding fault classes, collected when the engineering system was operating in a limited set of working conditions, and unlabeled data containing only signal measurements collected in an EE. Wavelet transforms and statistical indicators are used to extract features from the non-stationary measured signals, then, the feature set to be used for fault diagnostics in an EE is selected based on three indicators: 1) the classification accuracy and precision of a Support vector Machine (SVM) classifier, computed considering only the available labeled data; 2) the confidence of a SVM classifier trained using the available labeled data and tested on the unlabeled data collected in the EE; 3) the silhouette index of the classes obtained by SVM classifier considering the unlabeled data. Finally, a sparse Borda Count method is used to perform a multi-objective ranking of all the feature sets and, thus, to identify the one with the most satisfactory trade-off among the three indicators.
With respect to 2), an α surface reconstruction method is developed to detect the occurrence of drifts in the working conditions. Then, once a drift is detected, the diagnostic model is updated by using an approach based on the COMPacted Object Sample Extraction (COMPOSE) algorithm, which is firstly developed in the domain of stream data learning and is modified in this PhD work to fulfil the requirements of fault diagnostics. The improved COMPOSE algorithm allows identifying when it is really necessary to update the classification model due to the presence of a concept drift. A second novelty is an automatic procedure for setting the internal parameters of COMPOSE, in such a way that the size of the training set remains stable.
For the prognostics, a Particle Filter-Based approach has been developed for estimating the unknown effects of the working condition on the physics-based degradation model, and, simultaneously, predicting the Remaining Useful Life (RUL) of the engineering systems. The traditional particle filter is improved by using an Optimized Tuning Kernel Smoothing method, which is capable to overcome the problem of particle impoverishment and maintain the robustness of the degradation state estimation and RUL prediction.
Finally, a method for online assessing the performance of the RUL predictions has been developed to inform the maintenance decision makers on how confident they can be about the obtained prognostic results. This method requires the availability of i) signal measurement collected from the onset of the degradation trajectory until the present time on the degrading engineering system of interest and ii) a generic model-based prognostic approach based on the use of a Bayesian filter. The basic idea behind the on-line performance assessment method is to verify whether the predictions of the degradation state provided in the past have been accurate and precise. In particular, we consider past predictions of the degradation state on time horizons similar to the RUL predicted by the prognostic model at the present time, and we verify the performance of the RUL predictions performed in the past (from the beginning of component life to the present time).
Figure 1 shows an overview of the developed approaches and the methods on which they are based. Notice that both model-based PHM methods (Particle Filter, Kernel Smoothing, and Monte Carlo Simulation), and data-driven PHM approaches (Wavelet Transform, Statistical indicators,



1. Methods applied in this PhD work

Support Vector Machine, α surface reconstruction and COMPOSE) have been employed. The choice on the type of approach is motivated by the information available to deal with the problem. Different PHM applications have been considered to verify the proposed approaches: diagnosis of ball bearing defects and RUL prediction of Li-on batteries, turbine blades in energy production plants and aluminum electrolytic capacitor in fully electrical vehicles. The applications show that in case of modifications of the working conditions, namely in the presence of EE, the proposed PHM methods allow obtaining more accurate and precise diagnostics and prognostics results than the conventional PHM approaches.

ADVANCED CUBIC EQUATIONS OF STATE FOR ACCURATE MODELLING OF FLUID MIXTURES. APPLICATION TO CO2 CAPTURE SYSTEMS

Silvia Lasala - Supervisor: Prof. Paolo Chiesa

The target of reducing the worldwide level of greenhouse gases emitted by industries has diverted the focus of engineers and scientists towards the achievement of an increased efficiency of production processes, on the one side, and the design of innovative low-CO_2 emissions energy systems, on the other. In this context, new technologies have been developed to capture the CO_2 produced by energy-intensive industries, utilize and/or sequestrate it. Although more than twelve Carbon Capture and Storage (CCS) projects are already in operation or under construction, the current main obstacle to the further deployment of CCS is the requirement of large investments in capital equipment and high operating expenses. Many researchers have identified, in the inaccurate thermodynamic modelling of typical CCS multicomponent systems, one of the main sources of uncertainty for estimating costs associated to CCS. Depending on the fuels, the oxidant and type of CCS technology, captured CO_2 streams may contain different types and amounts of impurities, such as N_2, O_2, Ar, H_2O, CO, H_2, COS, SOx, NOx, CH_4 and H_2S. Thus, the PER comparison between the system model and the reference system has shown a better energy performance of the developed system for both the cooling dehumidification mode and the heating humidification mode. shows a classification of the types of impurities that can be present in the streams captured by the different developed capture technologies.

Mainly due to the complex thermodynamic modelling of these fluids, especially at high pressures, none of the thermodynamic models presented in the literature shows any clear advantage for both Vapour-Liquid-Equilibrium (VLE) and volume calculations. Aware of the low capability of each available equation of state in modelling any thermodynamic property, for whatever thermodynamic system treated in the CCS chain, engineers oversize the equipment, to ensure the achievement of capture requirements. Clearly, such an oversizing leads to more relevant investment and operating costs.

The original and final purpose of this thesis is to quantify the influence of the level of accuracy of a thermodynamic model in determining performances of key components of a CO_2 purification and compression unit and making considerations concerning its sizing. In particular, different CO_2-based mixtures are considered, as an input to these units, deriving from the use of various types of capture technologies (oxy-fuel, post-combustion or pre-combustion capture) in coal- or natural gas-fuelled power plants. This work aims at studying binary and multicomponent systems resulting from the combination of 9 components CO_2, H_2, N_2, O_2, Ar, CO, CH_4, H_2S, H_2O.

CLASS I	CLASS II	CLASS III
$CO_2 + H_2O$	$CO_2 + H_2O$ + non-combustible components (Ar, N_2, O_2)	$CO_2 + H_2O$ + non-combustible (Ar, N_2, O_2), combustible (CH_4, H_2, CO) and toxic (H_2S, CO) components
Typical capture processes: based on absorption separation methods	*Typical capture processes:* based on low-temperature phase separation methods and, eventually, membranes	*Typical capture processes:* based on low-temperature or absorption separation methods

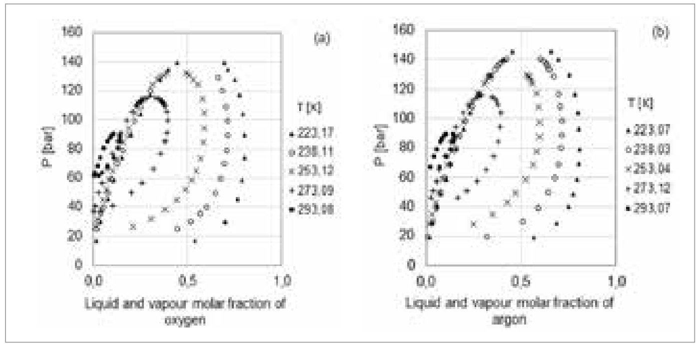
1. Classification of captured streams on the basis of their composition

To achieve this objective, three main topics are covered within this thesis: I – experimental analysis of thermodynamic properties of the considered systems; II – definition of an advanced cubic equation of state, being able to accurately represent the critical region of highly non-ideal fluids; III – application of this thermodynamic model to CCS systems. The content of these three parts is presented in the following, in more detail.

I. The analysis of experimental data available from the literature has shown that, among all vapour-liquid equilibrium measurements of non-toxic and non-flammable fluids, data for CO_2-O_2 and CO_2-Ar binary systems are insufficient to enable the optimization and/or validation of thermodynamic models. Similarly, multicomponent VLE data containing CO_2, N_2, O_2 and Ar are absent. Thus, an experimental campaign has been carried out to partially fill such gaps and experimental vapour-liquid equilibrium data are presented in this thesis for: (i) binary mixtures of CO_2-N_2, CO_2-O_2 (see Figure2-a), CO_2-Ar (see Figure 2-b), at 223, 238, 253, 273, 293 K ; (ii) ternary mixtures of CO_2-O_2-N_2 and CO_2-Ar-N_2 at 273K and 233K. A thorough analysis of measurement uncertainties of data is also presented in this part of the work.

II. Among available thermodynamic models, cubic EoS are the mostly applied by process engineers; and the reason for their widespread application lies in their recognized high capability and simplicity in modelling the thermodynamics of complex systems. Cubic EoS have been considered in this thesis also because, despite the copious amount of scientific works aimed at investigating and applying such models, some theoretical improvements can yet be implemented in the field of both pure and multicomponent fluid modelling. This is the second target of the thesis. Two classes of mixing rules are applied to the Peng-Robinson equation of state, that are based on two different assumptions: random mixing and non-random mixing (i.e. accounting for local composition effects). These mixing rules are, respectively, the *quadratic van der Waals mixing rules* and mixing rules derived by incorporating activity coefficient models in cubic equations of state, namely "*EoS+a^{γ}_{E} mixing rules*". Wilson and UNIQUAC activity coefficient models are applied. The Peng-Robinson equation of state, combined with both mixing rules, is optimized over VLE data of each binary system and validated over VLE and calorimetric data of both binary and multicomponent systems. The comparison between these three optimized models has led to the conclusion that the application of mixing rules based on the assumption of non-random mixing, *EoS+a^{γ}_{E} mixing rules*, enables the radical improvement of the phase behaviour modelling of non-ideal systems, in particular their critical region. Differently, van der Waals mixing rules are not able to accurately represent the high-pressure phase behaviour of these fluids and completely fail in describing their critical region.

III. These models are applied to evaluate performances of units for CO_2 purification (CPU), in Carbon Capture and Storage systems. Outcomes are then compared to assess the effect of the improved accuracy of the thermodynamic model on performance calculations and sizing considerations.



2. Experimental vapour-liquid equilibrium measurements of binary mixtures O_2-CO_2 (a) and Ar-CO_2 (b), presented in this work.

IMPROVEMENT OF THE CONTROL-ORIENTED MODELLING OF THE GEN-IV LEAD-COOLED FAST REACTOR: DEVELOPMENT OF REDUCED ORDER METHODS

Stefano Lorenzi

Supervisors: Prof. Antonio Cammi, Prof. Lelio Luzzi, Prof. Gianluigi Rozza

In the last years, the research in the nuclear field has focused on the Generation-IV reactors to reach high standard in the areas of sustainability, economics, safety and reliability, proliferation resistance and physical protection. Among these reactor concepts, the Lead-cooled Fast Reactor (LFR) seems promising due to the excellent material management capabilities, the plant simplification, and the higher operating efficiencies compared to other coolants, introducing however some safety concerns and design challenges. The need to investigate the control strategy for this innovative system arises from the fact that the new technological issues brought by the use of lead as coolant do not make possible the adoption of the classic approaches. In particular, the spatial dependence plays a relevant role in the dynamics evolution, both in neutronics and in thermal-hydraulics environment.
In the development of the control system, it is of primary importance to rely on simulation tools for its realization, testing and validation by means of an accurate description of the reactor-controlled response. The classic control-oriented approach based on 0D/1D modelling is appropriate whether the spatial effects are not relevant and only the estimation of integral quantities is required as for the Single Input Single Output (SISO) control laws. On the opposite side, the 3D modelling is usually devoted to design purposes having a high level of detail but extremely expensive from a computational point of view. In the light of the previous considerations, the research efforts should be devoted to combine a high-detail modelling featuring spatial capabilities (e.g., 3D modelling) with the requirements demanded for a control-oriented tool, firstly the computational efficiency.
A viable solution is to employ Reduced Order Modelling (ROM) techniques. Reduced order modelling is a generic expression to identify any approach aimed at replacing a high-fidelity problem, i.e., the Full Order Model (FOM), by one featuring a much lower computational complexity, i.e., the reduced order model. The main assumption of ROM is that the behaviour of the system with respect to a parameter (physical, geometrical) or the time can be represented by a small number of dominant modes. In this way, the system evolution is represented by a reduced set of ordinary differential equations. The latter can be employed, for instance, as the basis for the synthesis and the verification of controllers.
The Ph.D. work seeks to improve the control-oriented modelling of Generation IV LFRs through the development of reduced order methods. In the thesis, the reference reactor is ALFRED (Advanced Lead Fast Reactor European Demonstrator), a pool-type reactor whose conceptual design was developed within the Euratom LEADER Project. The reduced order models are aimed at being assessed and implemented in an object-oriented simulator developed with the Modelica language, in the Dymola environment. In particular, the attention is focused on the neutronics and the thermal-hydraulics of the reactor pool, substituting the modelling components based on zero-dimensional approach with ROM-based models. The aim is to provide the control-oriented simulation with a better physical description and a high modelling accuracy without increasing the computational burden.
As for the neutronics, a spatial model for the reactor core has been developed. This approach is directed to go beyond the classic Point Kinetics (PK) currently used in control-oriented models due to the inability of such zero-dimensional method to allow for the spatial dependence of the flux. The spatial neutronics modelling has been developed considering different choices of spatial basis and test functions, based on the Modal Method (MM) and the Proper Orthogonal Decomposition (POD). The proposed approach is easy to implement in any control simulator environment, thanks to its matrix formulation and the derivation of the main variables of interest (power, flux, reactivity). The spatial neutronics approach has been tested in a simple 3D case. The results show that the proposed approach improves the modelling accuracy with respect to the classic PK, being the model capable to predict the reactivity evolution also in strong localized transients or relevant operational scenarios (e.g., shutdown). In addition, an object-oriented model of the 3D test case has been settled in order to prove the feasibility of employing ROM-based components in control-oriented simulators. As for the entire reactor core, a detailed model of the ALFRED reactor has been set up. Starting from the spatial basis and the test functions calculated solving the neutron diffusion equations, the MM has proved not to be suitable in case of Control Rod (CR) movement even if it works for thermal feedback effects. On the other hand, an Adjoint Proper Orthogonal Decomposition approach is proposed to merge the benefit of the POD spatial basis and the relevance of the adjoint flux as test function. This new approach has been tested in case of both thermal reactivity effects and CR movement, giving better results with respect to the classic POD approach.
As for the thermal-hydraulics, a spatial model of the reactor pool has been developed. This approach is directed to overcome the 0D/1D modelling usually employed in control-oriented models for the fluid dynamics. In particular, the 0D/1D approach prevents the simulation tool from taking into account the spatial features of the fluid flows, which can be relevant for certain reactor systems. As first step to provide the object-oriented simulator with a ROM-based component representative of the ALFRED coolant pool, a POD-Galerkin Method for Finite Volume Approximation of Navier-Stokes and RANS equations has been developed (POD-FV-ROM). The aim of this new ROM approach is both to extend the classic POD-Galerkin-ROM method to the Finite Volume approximation of the Navier-Stokes equations and to build a reduced order model that is capable to handle turbulent flows modelled through the RANS equations. The reason behind this effort is to pursue the classic approach used in nuclear engineering for the turbulent flows based on the Finite Volume approach. Since for the control-related applications the RANS equations are sufficient to describe the main time-averaged properties of the flow (velocity, pressure, stresses), the focus has been oriented to turbulence modelling such as the eddy viscosity models. The POD-FV-ROM is tested in the classic benchmark of numerical simulations for the 2D lid-driven cavity. In particular, two simulations at Re = 1000 and Re = 100000 are considered in order to assess both a laminar and turbulent case. The comparison between FOM and ROM has turned out to be very satisfactory as well as the time performance.
Starting from the proposed procedure, a parametric ROM-based component of the coolant pool of the ALFRED reactor has been developed. In order to demonstrate the possibility to employ a ROM-based component in a control-oriented simulator, the possibility to vary the input variables of the model has been undertaken. In particular, the lead velocity at the SG outlet has been considered as parametrized boundary condition since it can be a possible control variable. The simulation results show a good agreement between the ROM and the FOM in reproducing the velocity field up to 50% variation of the lead velocity at the SG outlet with respect to the nominal value. As a major outcomes of the ROM, it has been proved that its behaviour is more accurate than 0D model without an excessive computational cost.
The thesis shows the advantages and the feasibility to employ ROM-based components in control-oriented simulators. Finally, the proposed approach and modelling techniques can be applied to different reactor concepts.

LASER CLEANING OF DIAGNOSTIC FIRST MIRRORS FOR NUCLEAR FUSION MACHINES

Alessandro Maffini - Supervisor: Prof. Matteo Passoni

The main objective of my Ph.D thesis was the study of the laser cleaning technique as a potential solution for the cleaning of diagnostic first mirrors in nuclear fusion systems.
Thanks to its capability of producing energy on a large scale, using cheap and abundant fuels with a negligible level of greenhouse emissions, nuclear fusion power is the most attractive long-term solution to the energy needs of human civilization.
Outstanding scientific and technological challenges must be faced in order to ensure develop an operative fusion reactor, many of which are related to the interaction between the thermonuclear plasma and the materials and components that constitute the reactor first wall.
The essential task of controlling the plasma will require a large number of optical diagnostics, i.e. systems that analyze the electromagnetic radiation emitted or scattered by the plasma.
Light coming from the plasma will be guided towards the data acquisition system through a chain of optical elements. The most critical components will be the mirrors directly facing the thermonuclear plasma, known as First Mirrors (FMs). Due to the interactions with the plasma, FMs are subjected to different phenomena that can dramatically affect their reflectance. Among them, the re-deposition on their surface of material eroded elsewhere from the tokamak first wall is considered the most threatening issue to FMs lifetime and performances, as shown by different mirror exposure campaigns that have been carried out in present-day tokamaks.
To tackle this issue, the implementation of suitable in situ mirror cleaning solutions is required also in a test reactor like ITER (scheduled for the 2020s), and therefore represents a necessary step towards the development of fusion power plants.
Ideally, a FM cleaning technique should be compatible with reactor environment, safe for the mirror integrity, fast and effective for different kinds of contaminants. Laser cleaning is considered one of the most promising solution.
The results of the few laser cleaning trials attempted so far on FMs have highlighted that the inherent complexity of laser cleaning physics, the sensitivity of mirror surface to laser damaging and the dependence of optimal cleaning parameters on the characteristics of the re-deposits are crucial issues to be addressed.
This PhD thesis aimed at addressing these open issues with a systematic experimental approach that makes use of lab-scale equipment and techniques.
The goal of this thesis was threefold: to get a better comprehension of the physics of the laser cleaning process, with particular attention to the role played by cleaning parameters with respect to the re-deposit properties; to develop a reliable and robust cleaning procedure, which can effectively recover the reflectance of the mirrors while preserving their integrity; to assess the feasibility of the laser cleaning technique in a reactor environment.
The main objective of my Ph.D thesis was the study of the laser cleaning technique as a potential solution for the cleaning of diagnostic first mirrors in nuclear fusion systems.
Thanks to its capability of producing energy on a large scale, using cheap and abundant fuels with a negligible level of greenhouse emissions, nuclear fusion power is the most attractive long-term solution to the energy needs of human civilization.
Outstanding scientific and technological challenges must be faced in order to ensure develop an operative fusion reactor, many of which are related to the interaction between the thermonuclear plasma and the materials and components that constitute the reactor first wall.
The essential task of controlling the plasma will require a large number of optical diagnostics, i.e. systems that analyze the electromagnetic radiation emitted or scattered by the plasma.
Light coming from the plasma will be guided towards the data acquisition system through a chain of optical elements. The most critical components will be the mirrors directly facing the thermonuclear plasma, known as First Mirrors (FMs). Due to the interactions with the plasma, FMs are subjected to different phenomena that can dramatically affect their reflectance. Among them, the re-deposition on their surface of material eroded elsewhere from the tokamak first wall is considered the most threatening issue to FMs lifetime and performances, as shown by different mirror exposure campaigns that have been carried out in present-day tokamaks.
To tackle this issue, the implementation of suitable in situ mirror cleaning solutions is required also in a test reactor like ITER (scheduled for the 2020s), and therefore represents a necessary step towards the development of fusion power plants.
Ideally, a FM cleaning technique should be compatible with reactor environment, safe for the mirror integrity, fast and effective for different kinds of contaminants. Laser cleaning is considered one of the most promising solution.
The results of the few laser cleaning trials attempted so far on FMs have highlighted that the inherent complexity of laser cleaning physics, the sensitivity of mirror surface to laser damaging and the dependence of optimal cleaning parameters on the characteristics of the re-deposits are crucial issues to be addressed.
This PhD thesis aimed at addressing these open issues with a systematic experimental approach that makes use of lab-scale equipment and techniques.
The goal of this thesis was threefold: to get a better comprehension of the physics of the laser cleaning process, with particular attention to the role played by cleaning parameters with respect to the re-deposit properties; to develop a reliable and robust cleaning procedure, which can effectively recover the reflectance of the mirrors while preserving their integrity; to assess the feasibility of the laser cleaning technique in a reactor environment.
morphology, ensuring a good reflectance recovery in the Vis-NIR region for all the samples considered. On the contrary plasma cleaning failed to restore mirror reflectance when porous contaminants were involved. Nevertheless, in the case of compact W/O contamination, plasma cleaning allowed to recover also the UV reflectance, which could not be restored by means of laser cleaning.
As far as mirror integrity is concerned, laser cleaning proved to be gentler than plasma cleaning treatment. In addition, laser cleaning treatment was much faster than plasma cleaning (tens of minutes instead of several hours).
These results confirm that laser cleaning is definitely a valuable and feasible option for the cleaning of diagnostic FMs also in comparison with plasma cleaning, the most investigated solution so far.
A natural continuation of this Ph.D project envisages the realization of benchmark laser cleaning tests on mirrors exposed in operating tokamaks.
Taking advantage of the systematic results gathered in this thesis, one should be able to choose the best cleaning procedure to treat the mirrors contaminated by tokamak re-deposits. A successful achievement in this respect would validate the lab-scale approach hereby followed, marking an important step towards the development of a cleaning solution for FMs in fusion reactors.
Finally, the encouraging results here summarized can also be useful to design and engineer a laser cleaning mock-up which is realistic in the view of ITER.

FUNCTIONAL PROPERTIES CONTROL OF DOPED TiO_2 FOR TRANSPARENT ELECTRODES AND PHOTOANODES

Piero Mazzolini - Supervisor: Prof. Andrea Li Bassi

Co-supervisor: Prof. Carlo S. Casari Tutor: Prof. Carlo E. Bottani

The evolution of **new generation solar cell devices** requires the discovery and optimization of novel and more performing solutions in terms of materials and cell architectures, but also a perfect match among the several material interfaces which constitute the device. In this framework, the thorough study focused on the control and understanding of the optical and electrical properties of **Ta-doped TiO_2 (TaTO)** thin films discussed in this thesis work is of particular relevance.
Because of its transparency to visible light, high chemical stability in reducing atmosphere and proper band alignment with respect to the photo-active components of the solar cells, **undoped TiO_2** is one of the most employed materials in several photovoltaic device architectures (e.g. dye sensitized or perovskite-based solar cells). In particular, it represents an efficient and selective bridge for the separation and transport of the photogenerated electrons throughout the anode side of the device. A well suited energy level alignment *(i)* with the photoactive material (which actively generates the electron-hole couples) in the form of a high surface area porous layer ("**photoanode**"), and *(ii)* with the front electrode (which has to finally collect the electrons) in the form of a compact and continuous film ("**selective layer**") is the basic requirement for the best functioning of the device. All the materials at the anode side of the device must be characterized by high transmittance to the visible light. Consequently, the front electrode has to combine both transparency and conductivity; for this purpose, a material in the class of **Transparent Conductive Oxides (TCOs)** is usually employed. Nonetheless, the most performing TCOs (indium-tin oxide – ITO, fluorine-doped tin oxide FTO) can result in an unfavorable matching of the energy levels with respect to TiO_2 (photoanode/selective layer – TCO interface), eventually causing a considerable reduction in the overall performances of the device. Interestingly, in 2005 donor-doped TiO_2 (e.g. TaTO) has been proposed as a new class of TCOs. In fact, the substitution of a certain amount of Ti atoms in the anatase TiO2 cell with donors leads to the promotion of a large amount of electrons in the conduction band, resulting in low electrical resistivity while maintaining a good transmittance. The ability of controlling the electrical properties of TiO_2 is an extremely appealing opportunity for all the components of the anode of the cell (TCO + selective layer + photoanode), which could open up to an unprecedented all-TiO_2 based architecture with a perfect alignment of the energy levels among the device interfaces. However, the attainment of a fine control of the functional properties of TaTO thin films on cheap substrates (e.g. glass) is still an open issue and a basic requirement for the future application of TiO_2-based TCOs. For these reasons, the main goal of this thesis work was the synthesis and characterization of polycrystalline TaTO thin films, with the aim to unveil the full potentialities of this material as a TCO/selective layer and photoanode. A particular focus is made on the physical mechanisms which are ruling the functional properties of the material (i.e. conductivity and transparency), since this represents an open and debated issue in the scientific community.
The synthesis of TaTO and TiO_2 polycrystalline films was accomplished by room temperature **Pulsed Laser Deposition (PLD)** on soda-lime glass substrates followed by an annealing cycle in order to crystallize the initially amorphous films in the anatase phase. Taking advantage of the high control and versatility of the PLD technique, I developed the ability to finely control the morphology of the samples by tuning the oxygen background pressure (p_{O2}) during the laser ablation process. In particular, *(i)* compact (p_{O2} = 1 – 2.5 Pa) as well as *(ii)* "nano-tree" shaped porous films (p_{O2} = 10 – 15 Pa) were obtained with several extrinsic doping concentrations (Ta = 0, 1, 5, 10 at.%). This ability opened to the optimization of the material properties for a *(i)* TCO-selective layer and a *(ii)* photoanode application.
The best TCO functional properties (resistivity **$\rho \sim 5 \times 10^{-4}$ Ωcm**, mean transmittance in the visible range **T_{vis} > 80%**) were obtained for compact TaTO samples (Ta = 5 at.%) deposited at p_{O2} = 1 Pa and subsequently crystallized with a "standard" vacuum annealing (T = 550°C, ramp 10 °C/min). Notably, the possibility to finely tune the electrical properties of TaTO compact films was independently achieved for *(i)* different extrinsic dopant concentrations, and *(ii)* different oxygen partial pressures during the room temperature deposition process while maintaining a fixed Ta-doping level. In both cases it was demonstrated the ability to vary the charge carrier density in a wide range (**$n \sim 10^{19} – 10^{21}$ cm^{-3}**), making TaTO appealing for both TCO and selective layer application. These results were discussed in light of the ability to control the material structure at the atomic scale with the formation of several point defects (e.g. O and Ti vacancies) as a function of the oxygen partial pressure during deposition and/or the subsequent annealing process.
In the case of the post-deposition thermal treatment it was found that even the presence of some parts per million of oxygen in the annealing atmosphere resulted in the obtainment of highly insulating films. Nonetheless, it was demonstrated the possibility to overcome this limit via **Ultra-Fast annealing processes (UFA)**. Notably, these treatments are reducing temperature (from 550 °C to 460 °C) and time needed to accomplish a complete crystallization of the sample (180 min vs. 5 min) with respect to a standard thermal cycle. It is noteworthy that UFA performed in a cheap nitrogen atmosphere lead to TaTO and TiO_2 films with the very same resistivity and transparency obtained with a standard vacuum treatment.
A study on the **electrical properties of "nano-tree" shaped porous films** was also conducted in order to investigate on the possibility to increase the electron conductivity along the vertical direction of these nanostructures for a photoanode application. The electrical measurement of these films required unconventional contactless techniques. Experiments employing a synchrotron light source permitted to find that, similarly to what has been found for the compact films, the incorporation of different concentrations of Ta in the anatase matrix resulted in an increased and tunable conductivity of the nanotrees.
Moreover, a thorough study of the structure – property relationships was done with **XRD** as well as **Raman** spectroscopy. A significant trend between the anatase unit cell parameters and the synthesis conditions (i.e. the electrical properties) was established. Nonetheless, it is noteworthy to mention the solid relationship that was found between the shift of the most intense anatase Raman active mode *Eg*(1) and the corresponding charge carrier density. With the aim of shedding light on the point defects involved in this electrical / structural trends, a **Positron Annihilation Spectroscopy** study was conducted. The direct comparison between electrically conducting and insulating TaTO films allowed to collect important and unprecedented experimental evidences on the defects which are ruling the material behavior.
Finally, combining the acquired knowledge on the synthesis and control of the functional properties of TaTO films it was possible to obtain multi-layer structures with the aim of realizing an **all TiO_2-based TCO + selective layer + photoanode**. This novel solution is currently under testing in new generation perovskite-based solar cells. These combined structures could be fundamental not only for a mere efficiency improvement of the device, but also for the investigation of the still debated physical mechanisms behind the superior performances of perovskite-based solar cell devices.

NOVEL *i*-SANEX/GANEX FORMULATION FOR HYDROMETALLURGICAL ACTINIDE SEPARATION FROM SPENT NUCLEAR FUEL

Eros Mossini - Supervisor and Tutor: Prof. Mario Mariani

Co-supervisor: Dr. Elena Macerata

Abstract

This Ph.D research deals with innovative hydrometallurgical approaches for actinides (An) recycling from Spent Nuclear Fuel (SNF). It was developed within the SACSESS (Safety of ACtinide SEparation proceSSes) project, promoted in the seventh Framework Program by the European Commission. The research was mainly focused on the investigation of radiochemical stability of two innovative hydrophilic ligands for the An selective separation. The experimental activity was mainly performed at *Politecnico di Milano*, in the Radiochemistry and Radiation Chemistry lab. Abroad research periods at ATALANTE lab (*Commissariat à l'Énergie Atomique et aux énergies alternatives*, CEA), Radiochemistry lab (Heidelberg University) and Nuclear Waste Management and Reactor Safety Department (*ForschungsZentrum Jülich*, FZJ) were funded by European scholarships.

Introduction

Over the 21st century, the energy demand is expected to increase. Nuclear energy could play a leading role in future strategy aimed at reducing greenhouse gases emission. In this context, SNF management is a major concern to be dealt with. Up to 2012, 360500 t of heavy metals has been globally discharged. Currently, two management strategies are considered. The open fuel cycle envisages the direct long-term disposal of SNF. Since SNF contains about 95% of uranium and 1% of other An, it is extremely radiotoxic for about 300000 years. The closed fuel cycle was proposed for a safer SNF management. It would allow recovering reusable materials to be burned in advanced nuclear reactors, thus obtaining shorter-lived or even stable nuclides and reducing the required storage time to few hundreds of years. To date, hydrometallurgical processes, such as the PUREX (Plutonium and Uranium Redox EXtraction) process, have been applied at industrial scale for the recovery of U and Pu isotopes. Furthermore, the feasibility of counter-current multistage processes for recycling of trivalent An was demonstrated. Two promising approaches are *i*-SANEX (innovative Selective ActiNide Extraction) and GANEX (Grouped ActiNide Extraction) processes. The key task is the separation of An from lanthanides (Ln), neutron poisons, due to their similar chemical behaviour. An and Ln are hard acids in the Pearson's theory. Ligands involving hard electron-donor atoms, such as O, electrostatically interact with An and Ln, without discrimination. An separation could become possible if soft electron-donor atoms, such as N and S, are grafted on the ligand complexing site. When developing a ligand for SNF reprocessing, several industrial constraints have to be fulfilled:

- selectivity towards An, *i.e.* strong affinity for An and low affinity for Ln;
- reversibility of An retention, *i.e.* easy An release;
- solubility in suitable diluent;
- fast complexation kinetics;
- no hydrodynamic problems, such as third phases and precipitates;
- stability towards hydrolysis and radiolysis;
- CHON principle, the ligand should contain only C, H, O, N atoms in order to be completely incinerable without generation of secondary solid waste.

To date, few promising hydrophilic ligands have been proposed, although none of them matched the requirements. In particular, the resistance towards hydrolysis and radiolysis is an undeniable key requirement in view of the scaling-up of advanced SNF partitioning. Therefore, when developing a novel solvent extraction process in the nuclear reprocessing field, the assessment of radiolytic robustness of all the chemicals involved is imperative. The experience gained from processes for U and Pu recovery, in operation since '60s, is rich in lessons learned about the potential consequences of radiolysis:

- deterioration of physico chemical properties (*i.e.* density, viscosity, precipitates formation);
- degradation of the solvent composition (*i.e.* consumption of the original ligand, production of ligand and diluent degradation by-products which may be themselves competitive complexing agents) resulting in performances worsening;
- alteration of extraction kinetics;
- change of redox properties of metallic ions by reactions with radical species.

Results

The novel ligands studied in this Ph.D. research involve N-heterocyclic atoms in the complexing site, with the purpose of obtaining a soft-donor electronic configuration affine to An. These complexing agents are CHON principle compliant and they showed promising selectivity for An joined with fast stripping kinetics. The assessment of the impact of hydrolysis and radiolysis on process safety and An separation efficiency was the main objective of this Ph.D. research project. In order to simulate the radiolytic damage delivered at reprocessing conditions, stripping solutions containing the hydrophilic ligand were irradiated at several absorbed doses and different dose rates by means of gamma radiation sources and subsequently analysed. The primary outcomes of the research were:

- evaluation of physico chemical radiolytic stability of the system, *i.e.* density, viscosity, acidity and nitrate anion concentration, because alteration of these properties of the solvent could seriously affect ligand-cation speciation mechanism and safety of future reprocessing plants;
- quantification of radiation induced ligand consumption by means of HPLC-DAD, with further confirmations by UV-vis, NMR and FT-RAMAN techniques;
- identification of radiolytic degradation by-products by means of NMR and HPLC coupled with ESI-MS, in order to evaluate if performance deterioration, due to potential solubility or complexation site alterations, could be expected from the hypothesised chemical structures of the degradation products;
- assessment of stripping solvent performances in *i*-SANEX and GANEX process-like conditions by means of batch liquid-liquid extraction tests after gamma irradiation at elevated absorbed doses (up to 200 kGy);
- characterization of complexation mechanism between the ligand and trivalent americium, curium and europium cations by means of UV-vis and TRLFS analyses on fresh, aged and irradiated solutions, in order to better understand the stripping solvent selectivity towards An, even in hydrolytic and radiolytic degradation conditions.

Moreover, since unprecedented stability towards hydrolysis and radiolysis was demonstrated, a valid approach for stripping solvent recycling was outlined. The system was proposed for testing on real waste in a multi-stage centrifugal contactor battery. With this purpose, the single-stage centrifugal contactor test is an undeniable preliminary step for single-stage efficiency calculation and flow sheet development. Thus, this experiment was successfully performed during the abroad research period spent at FZJ. It was shown that the proposed stripping solvent could ensure an adequately fast An selective stripping in presence of an organic phase loaded with synthetic PUREX raffinate.

Conclusions

This Ph.D. research experimental activity allowed demonstrating the excellent resistance of an innovative stripping solvent towards hydrolysis and radiolysis, in terms of An separation performances and of physico chemical stability. Several analytical techniques were exploited with the purpose of investigating the solvent radiolytic behaviour. In some cases, *ex-novo* developing of appropriate experimental procedures was required. The complexation mechanism with respect of trivalent Cm, Am and Eu was studied under hydrolysis and radiolysis degradation conditions. The reversibility of An retention by ligand recycling was proved as well as the applicability to industrial-like centrifugal contactor devices was assessed

PREDICTIVE MODELLING AND ADAPTIVE LONG-TERM OPTIMIZATION OF A HIGH TEMPERATURE PEM FUEL CELL BASED MICRO-CHP SYSTEM

Behzad Najafi - Supervisor: Dr. Fabio Rinaldi

Co-supervisor: Prof. Andrea Casalegno

Proton exchange membrane (PEM) fuel cell based combined heat and power (CHP) systems are recognized as promising alternatives for addressing electrical and thermal needs of residential buildings.
Low temperature PEM fuel cell (LT-PEM FC) is the most commonly used PEM technology for CHP applications; however, employing this type of stack results in many operational issues. High temperature PEM fuel cell (HT-PEM FC) technology has been introduced as a potential substitute to resolve these problems. Nevertheless, HT-PEM stacks suffer from a significant degradation which can have a considerable negative effect on the performance of the system. Therefore, this fact should be taken into account while investigating the performance of HT-PEM FC based CHP systems and attempting to improve their corresponding performance.
Accordingly, In the first step of the present thesis, an HT-PEM FC based configuration for an existing LT-PEM based CHP unit was proposed. Next, detailed physical phenomena based models, for all of the components, were developed and the developed models, employing the available experimental data, were validated. The validated models were subsequently integrated to determine the overall performance indices of the proposed. It was demonstrated that by employing the proposed configuration, an electrical efficiency of 29.1% can be obtained which is considerably higher than the efficiency of 21.4% achieved by the LT-PEM based system. Hence, it was evidently demonstrated that employing the proposed HT-PEM stack can significantly increase the performance of the system. Next, a parametric study was carried out in which the effect of key parameters of the fuel processor and the stack on the overall performance of the system was studied.
Considering the fact that the residential combined heat and power (CHP) systems should address intermittent load profiles, performance of the system while supplying different levels of electrical and thermal power, is of considerable importance. Hence, the subsequent step was dedicated to applying fuel partialization and power to heat shifting method for evaluating the performance of the system at a wider range of operation. In the fuel partialization strategy, the provided fuel was gradually reduced to 50% of its initial value and it was demonstrated that the generated electrical power is diminished from 27.6 kW at full load condition down to 15.8 kW while the thermal generation was reduced from 50.0 kW to 22.4 kW. In the second strategy, power/heat shifting, the imposed current of the stack was decreased, resulting in an increment in the anodic stoichiometric ratio, which in turn reduced the electrical power from 27.6 kW to 15.6 kW while the thermal generation, on the contrary, was enhanced by 6 kW. Finally, the mentioned strategies were combined and it was demonstrated that, employing the mentioned strategies, the system can provide a wide range of thermal and electrical generations.
In view of the fact that the preceding analysis does not guarantee the operation at optimal conditions, the subsequent step was devoted to employing multi-objective optimization method in order to determine the optimal operating points considering the electrical and thermal efficiencies as optimization objectives. The optimization procedure was carried out for full load and several partial load conditions in order to determine optimal operating points while covering a wide range of production levels. It was specifically demonstrated that, at full load condition, the highest achievable electrical efficiency is 29.5%.
Since the HT-PEM FC unit and the steam reformer reactor of the fuel processor suffer from a considerable degradation, the available experimental data was next utilized to develop a predictive model which can estimate the degradation in these components. The degradation estimation model was next integrated with the previously developed steady state model to simulate the long term performance of the system. It was demonstrated that, due to the degradation's effect, the power production of the plant, through the considered lifetime (15000 hours of operation), diminishes from 28.2 kW to 23.4 kW while the thermal generation increases from 52.4 kW to 57.5 kW. Next, two strategies were proposed and applied in order to remedy the excursion of thermal and electrical generation of the plant from their initial values.
The results of partialization strategy showed that, in order to confine the thermal generation amplification, the partialization factor should be increased up to 7.2 %. On the other hand, in the recovery strategy, the supplied fuel should be progressively increased up to 34.2% in order to preserve the electrical output at the initial level. Furthermore it was shown that, applying the recovery strategy has a significant adverse effect on the electrical efficiency as it results in the final electrical efficiency of 21.6 % compared to 24% obtained in normal operation. In the last step, the performance of the system obtained by normal operation and under proposed operational strategy was compared. It was shown that, the applying the partialization strategy not only keeps the thermal generation constant but also results in a minor improvement in the performance of the system as it increases the average cumulative electrical efficiency from 26.1% to 26.4%. It was also demonstrated that, as could be expected, applying the recovery strategy can result in an average cumulative electrical efficiency of 24.7% which is significantly lower than the value obtained using normal operations.
Although the previous strategies reduce the variations in the plant's thermal and electrical output , they do not assure operation at optimal operating conditions and do not provide useful information about the performance of the plant while addressing intermittent load profiles. Therefore, in the subsequent analysis, an attempt was made in order to adaptively optimize the operating conditions of the plant taking into account the gradual variation in the behaviour of the plant due to the degradation. The optimization was consequently carried out in 6 different time steps while providing a certain range of thermal or electrical production. Accordingly, in the first optimization procedure, thermal generation and electrical efficiency (indicating the system's performance) were considered as optimization objectives. A series of Pareto fronts were obtained including optimal points resulting in the highest possible electrical efficiency while generating certain thermal output at a specific time step. The achieved results demonstrated that by employing the obtained optimal points, beside keeping the thermal generation constant, the cumulative electrical efficiency of the system can be increased from 26.1% to 27.4%. Hence, it could be concluded that employing the obtained optimal operating conditions is a significantly more efficient approach compared to applying the partialization strategy.
Finally, an additional activity dedicated to economic optimization of the plant was carried out considering long-term cumulative efficiency and capital cost as objective functions. It was demonstrated that an attempt to achieve the highest possible efficiency results in an optimal point with the cumulative electrical efficiency of 29.96% while requiring a capital cost of 115711 €. The optimal point with the lowest required capital cost (39929 €) leads to a cumulative net electrical efficiency of 18.36%. Finally, it was demonstrated that by employing an optimal point in which the same fuel cell area as that of initial design is utilized, a cumulative net electrical efficiency of 27.07% can be obtained which is almost 1% higher than the one which was obtained using the initial design.

SILICON MICRODOSIMETRY IN HADRON THERAPY FIELDS

Eleni Sagia - Supervisor: Prof. Stefano Agosteo

Tutor: Prof. Andrea Pola

Hadron therapy is one of the most sophisticated methods of radiation therapy that has been constantly evolving during the past decades. The use of hadron beams for cancer treatment can be more effective in comparison to the conventional radiotherapy, due to the high ballistic precision and the high biological effectiveness of the particles. The implementation of the hadron beams in cancer therapy raised the need of establishing protocols for the dosimetric characterization of the beams for therapeutic precision and radiation protection. Several attempts to provide standards and protocols for hadron therapy based on the conventional dosimetric approach were proved to be insufficient, since an average quantity such as the absorbed dose cannot provide information on the biological effects of the hadron beams that are strictly related to the local distribution of the energy deposited at micrometric scale. The microdosimetric approach of the characterization of hadron beams intends to cover this gap and provide information of all beam properties, both physical and biological.

Tissue–Equivalent Proportional Counters (TEPCs) are the main detectors used to perform microdosimetry for assessing the beam quality in hadron therapy. However, there are several problems and limitations in the use of TEPCs, such as distortions of microdosimetric distributions due to wall effects and paralyzation of the detector at high flux fields because of pile-up effects associated to high count rates. These drawbacks in addition to the lack of transportability and ease of use, mainly due to the need of a continuous tissue–equivalent gas flow system, encourage the seeking for alternative methods, such as silicon microdosimetry.

A silicon microdosimeter, based on the monolithic silicon technology, was proposed during the past decade, by the Laboratory of Nuclear Measurements of "Politecnico di Milano" for hadron therapy applications. The device was irradiated with a 62 MeV clinical proton beam at the "Centro di AdroTerapia e Applicazioni Nucleari Avanzate" (CATANA) facility of the "Istituto Nazionale di Fisica Nucleare" (INFN) – "Laboratori Nazionali del Sud" (LNS) (Catania, Italy) and a 100 MeV pulsed proton beam at the Loma Linda University Medical Centre (California, USA). The results of these measurements confirmed the detector's capability of characterizing a therapeutic proton beam.

Preliminary measurements with a 62 AMeV carbon ion beam were also performed at the CATANA facility.

The aim of this thesis was to investigate the capability of characterizing a heavy ion beam with a silicon prototype device and its' geometrically varying versions.

Supplementary measurements were carried out at the CATANA facility with a 62 AMeV carbon ion beam, under the same experimental conditions with the preliminary measurements performed in the past, in order to ensure reproducibility. Previous results were used to compare and confirm the consistency of the new results and additional sets of measurements completed the characterization of this field. The results of this experimental campaign for some common points were compared with the ones of the preliminary measurements performed in the past and found in agreement. Finally, the microdosimetric profile and the characterization of the irradiation field were completed by summarizing all sets of measurements.

A comparison of the numerical and experimental study carried out to characterize a 290 AMeV carbon ion beam at the Heavy Ion Medical Accelerator in Chiba (HIMAC) facility (Chiba, Japan). A comparison between the response of two different versions of the silicon device to the same field and a comparison of the detector response to two different fields (monoenergetic and clinical) of the same energy are also included. The numerical results were compared and found in agreement with the experimental data, confirming the consistency of the results and enhancing the confidence on the detectors' performance in high energy and flux hadrontherapy fields.

Preliminary measurements aiming to demonstrate the silicon detector capability of characterizing a therapeutic carbon ion beam in comparison to the one of a TEPC were performed at the "Centro Nazionale di Adroterapia Oncologica" (CNAO) facility (Pavia, Italy) with a 362 AMeV clinical carbon ion beam. Measurements were carried out with a mini – TEPC by INFN – "Laboratori Nazionali di Legnaro" (LNL), under the same experimental conditions, enabling the direct comparison of the results. These measurements are among the first microdosimetric measurements performed in therapeutic carbon ion field and the first that are carried out together with the reference detection system. The results of the comparison between the microdosimetric spectra derived with the two detection systems were considered to be satisfactory and the detector capability is confirmed. Minor deviations that occurred could be due to uncertainty in the precision of positioning of the two detectors (their dimensions are of different order of magnitude with the silicon detector being in μm while mini TEPC in mm) and to uncertainties induced by possible geometrical differences related to the chord length distribution in the sensitive volumes. Also, for this particular set of measurements the superiority of the TEPC concerning the minimum detectable energy does not seem to affect the final result. Due to the small number of measuring positions though, it is not safe to draw any conclusions concerning this issue and therefore supplementary measurements are recommended.

In conclusion, the capability of the silicon detectors to acquire microdosimetric spectra similar to those obtained with a reference microdosimeter has been confirmed, especially with the experimental campaign at the CNAO facility where a direct comparison was made. However, all results (including the ones of the mini-TEPC) were carried out at beam currents about two orders of magnitude lower than clinical ones, due to signal saturation and pile-up effects. Still, the irradiations in such high energy and flux fields provided useful information on the detector behavior that concerns the charge collection by the pixels guards. These indications require further investigation and could be the subject of future research.

In seek of other potential microdosimetric applications of the silicon microdosimeter, its latest version was irradiated with a 70 MeV carbon ion beam in vacuum at the Heavy Ion Accelerator Facility of the Australian National University. The device was irradiated for the first time in the context of an experiment aiming at better understanding the radiobiological effectiveness of a therapeutic carbon ion beam in the distal part of the Bragg peak and estimating the quality factor of carbon ions only with minimal fragment contribution. The outcome of this primary test, based on the successful execution of the experimental procedure and to the good experimental results was considered to be satisfactory. Nevertheless, a feasibility study is necessary to be conducted in the future and additional irradiations are recommended for a more detailed analysis of the new detector's behavior and performance, especially focusing on the possible impact of the modifications of the new version device might have.

NEUTRON DOSIMETRY AND SPECTROMETRY IN COMPLEX RADIATION FIELDS USING CR-39 TRACK DETECTORS

Alvin Sashala Naik - Supervisor: Dr. Stefano Agosteo

Tutor: Dr. Marco Caresana

The non-ionizing radiations which are neutrons tend to be a significant problem for radiation protection as compared to directly ionizing radiation (alpha, beta, heavy ions); indeed neutrons tend to be more penetrating in the human body. Through stochastic effects neutrons may induce cancer in any organs of the human body as they undergo nuclear reactions with the high hydrogen content materials such as the human tissue. Protection against thermal and epithermal neutrons is quite straightforward as they can be easily absorbed in a reasonable thickness of moderating material such as polyethylene, polystyrene or water (high hydrogen content materials). However, fast neutrons present a greater danger. The cross-section of those higher energy neutral particles tends to decrease with an increase in their energy or momentum. Thus, very thick walls (up to 2 m) of special types of concrete are needed around nuclear facilities generating those high energy neutrons in order to stop them. Even then, leakage of fast neutrons around high energy physics facilities is quite common and presents a subsequent danger. Furthermore, the relative biological effectiveness (RBE) associated to fast neutrons (100 keV to 20 MeV) shows a maximum compared to the RBE of other types of radiation; which means that one fast neutron can cause greater damage to the DNA than any other types of radiation. Thus the personnel working in environments where fast neutrons are typically generated in the form of a complex radiation fields around the nuclear device are particularly vulnerable. Currently, most national regulations are based on the 1991 ICRP Recommendations in Publication 60. International standards, such as the International Basic Safety Standards, various international labour conventions, and European directives on radiological protection are also based on these recommendations even if an update has been implemented later in 2007 through the ICRP Publication 103.

The executive PhD is performed within the ARDENT European project, managed by the CERN and funded by the 7th framework program through the Marie Curie Initial Training Network (ITN) Fellowships. The research objectives are defined by the work package 3 (WP3) of the ARDENT project. The goal of the WP3 is the development of CR-39 track detectors for neutron dosimetry and spectrometry in complex radiation fields. The project is pursued at Mi.am S.r.l and at the Politecnico di Milano using the Politrack™ automatic track detector reading system. This automatic microscope is currently used on an industrial scale for the analysis of CR-39 detectors exposed to radon gas to measure exposure in houses or workplaces. The upgraded version of the Politrack™ has been developed for neutron dosimetry and LET spectrometry, which is the main focus of the PhD. The reading procedure has been optimized in order to maximize the measurement accuracy. The etching technique, which allows to reveal the tracks formed at the surface of the CR-39 plastic when a particle has hit this surface, has also being optimized concurrently to the measurement campaigns. The Politrack instrument was developed at the Politecnico di Milano and has been optimised for neutron dosimetry and LET spectrometry using CR-39 detectors. The final fully operational system is currently being tested at Mi.am S.r.l, the private company marketing the industrial system. The CR-39 track detectors are commercial detectors available from RTP Company (U.S.A), which was formerly Intercast S.r.l (Parma, Italy). Yet, for our research work, Intercast S.r.l produced custom designed CR-39 detectors specifically suited for our research purposes. The radiation sources and beams used during the PhD project are facilities located around the globe, mainly: CERN (Switzerland), CNAO (Pavia, Italy), IRSN (France), PTB (Germany), iThemba labs (South Africa), INFN (Catania, Italy), Lawrence Berkeley National Laboratory (USA) and UC Berkeley (USA). A specific research innovation based on the 2-D neutron beam imaging is detailed in section, which was an outcome of a close collaboration with the UC Berkeley and Berkeley labs (LBNL).

The Monte Carlo simulation used is the FLUKA particle transport code which were provided free of charge by the CERN (Europe). The numerical research work is supervised by Dr. Sofia Rollet (Austrian Institute of Technology – AIT Vienna) and Dr. Michele Ferrarini (Fondazione CNAO, Pavia). The goal being to create a tool which will be used to design fast neutron dosimeters in the future, without necessarily doing systematic calibration campaigns in mono-energetic neutron beams; hence reducing considerably the overall production time and cost.

To conclude this summary, a comprehensive study of the capability of performing accurate neutron dosimetry based on the LET_{nc} spectrometry method has been performed in this PhD research work. Firstly, the dose equivalent measurements in workplace fields such as at the CERF tend to show that the final dose measured is in agreement with predictions within a 15 % margin of error, which stands as excellent compared to the current industrial neutron dosimetry standard error of around 50 %.

In addition, the simulation code which was developed during these 3 years research work, will be used for designing future prototypes of neutron dosimeters, even if a fair amount of research work has still to be investigated in the correlation between simulations and experimental results. The full development of such a simulation capability would provide a tool to characterise innovative dosimeters without the need for expensive irradiation experiments. The calibration can then be performed only during the final phase of the design, thus, reducing production time and cost. From a hardware point of view, the Politrack system can be further enhanced by optimising the optical system.

By implementing upgrades to the different components, the diffraction limit of the optical system can be reduced and tracks having diameter less than 8 μm from recoil protons could be measured by greater precision. Hence, improving the accuracy in the LET_{nc} spectrometry method for low-LET ionising particles producing these small tracks.

Using Monte Carlo simulations, an extensive research work is still required to understand some unanswered questions about the CR-39's LET response and angular response to different type of ionising radiation. Yet, the results from the LET spectrometry experiments and neutron dose measurement tend to prove the validity of the LET_{nc} spectrometric method used to evaluate the dose associated to the fast neutron component of a complex radiation field using CR-39 track detectors. Furthermore, from an innovation point of view, the 2-D neutron beam imaging capability can be considered as a very useful achievement from this PhD research project. In this perspective, further experiments will be carried out on HFNG experiment and the interesting results promise to give a tangible publication in the near future, in collaboration with the UC Berkeley and the Lawrence Berkeley National Laboratory.

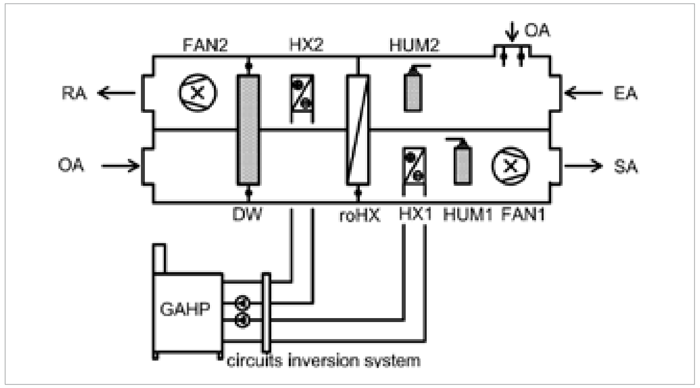
MODELLING AND EXPERIMENTAL EVALUATION OF A DOUBLE EFFECT THERMAL DRIVEN AIR CONDITIONING SYSTEM USING AMMONIA/WATER ABSORPTION AND DESICCANT EVAPORATIVE COOLING

Rossano Scoccia - Supervisor: Prof. Mario Motta

Tutor: Prof. Livio Mazzarella

A thermal driven air-conditioning system, worked out coupling two sorption cycles, has been developed. The goal is to develop a thermal driven primary air conditioning system, which is energy efficient, compact, reliable and without an auxiliary heat rejection system. The motivation is to reduce the non-renewable primary energy consumption of the air-conditioning sector and to increase the share of thermal driven system.
The system (Figure 1) integrates an absorption heat pump cycle and a solid desiccant evaporative cooling open cycle (DEC).

The system main feature is the ability of the absorption heat pump to drive a DEC cycle, creating a double effect thermal driven cycle.
After a compatibility analysis on the temperature levels an ammonia/water absorption heat pump and a silica-gel desiccant wheel have been selected.
The solid DEC cycle is implemented in a double duct air handling unit. In one duct the building supply air flows, while in the other the exhaust air from the building flows.
The system is able to work in seven operation modes according to the supply air set-point and the boundary conditions. The main operation modes are the cooling and dehumidification mode and the heating and humidification mode.
In cooling and dehumidification operation mode, the heat pump has two useful effects: it delivers the heating power needed to the desiccant based dehumidification process and it provides cooling power for the supply air flow.
In heating and humidification mode. The hydraulic connections between the DEC air handling unit and the heat pump is inverted, and the latter is used to heat up the supply air, recovering energy from the indoor exhaust air.
In order to assess the energy performance both an experimental analysis and a numerical modelling of the system have been done.
The experimental analysis task has started with the set-up of a new laboratory and of a system prototype and it has ended with an extended test campaign.
The prototype is composed by a DEC air handling unit with a nominal air flow rate of 5000 m^3/h and a gas fired ammonia/water absorption heat pump with a nominal heating power of roughly 40 kW. The DEC cycle is implemented in the air handling unit through a wetted media humidifier, a rotary heat exchanger, a finned tube air-water heat exchanger and a silica gel-desiccant wheel.



1. Air-conditioning system scheme. OA: outdoor air; EA: exhaust air; SA: supply air; RA: return air; DW: desiccant wheel; HX: heat exchanger; roHX: rotary heat exchanger; HUM: humidifier; GAHP: gas absorption heat pump

About the experimental laboratory realization, it is mainly composed of two air handling units, two water storages and a monitoring and control system. The first aim of the lab is the conditioning of two air flows according to the set-point condition (temperature, humidity by mass, air flow rate). The second aim is to control and monitor the energy performance of the prototype under tests.
Thus, a test campaign has been done. Most of the tests have been done for the cooling and humidification operation mode changing the external air inlet conditions in the range 26-35 °C and 10-16 g_w/kg.
The results have confirmed most of the expectations about the system energy performance. It has a good primary energy ratio (PER) for external air cooling and dehumidification, but the tested configuration cannot dehumidify the air more than roughly 5 g_w/kg.
The numerical modelling task has started with a simplified model for the design of the prototype and it ended with a model which has been tuned with the experimental results and completed with the definition and implementation of a control strategy.
The ratio between the net supply air energy exchange and the non-renewable primary energy used by the system (PER) has been assessed as the main performance figure.
As reference system for PER comparison an air-conditioning system composed by an air source electric heat pump, a gas boiler and a cross-flow air heat recovery has been considered.
Thus, the PER comparison between the system model and the reference system has shown a better energy performance of the developed system for both the cooling dehumidification mode and the heating humidification mode.
A system drawback is that the exhaust air heat recovery has to be limited for external air temperature lower than roughly 6 °C in order to avoid humidity freezing on the heat exchanger linked to the absorption heat pump evaporator.
Afterwards, an advance analysis of the absorption cycle has been carried out. It has involved an upgrade of the experimental set-up and an extension of the experimental tests. Thus, a model of the absorption cycle has been developed and tuned with the experimental data. The results revealed that the operating conditions of the cooling and humidification operation mode do not fit with the ability of the tested heat pump (based on a GAX absorption cycle) to operate with an energy efficiency higher than the single stage cycle.
It is concluded that a thermal driven air conditioning system has been successfully realized, modelled and tested. It is particularly suitable in areas where the natural gas is cheap and/or the electric energy generation and distribution system is weak.

ADVANCED TECHNOLOGIES FOR CO_2 CAPTURE AND POWER GENERATION IN CEMENT PLANTS

Maurizio Spinelli - Supervisor: Matteo Romano

Tutor: Stefano Campanari - Advisor: Stefano Consonni

The global concern around climate change is currently inspiring new efforts in the research of promising solutions for the mitigation of global warming, which is now understood to be trigger for several serious and global risks. According to all the scenarios depicted by climate models, if the current GHG emission will follow the same trend showed during last century, the increase in global warming will leave to our systems few possibility of adapting to the climate change consequences.
The energy sector is the first engaged in the research topic of climate change and CO_2 emissions, and now it is dealing with the challenge of pushing the electricity production towards a horizon of green and efficient technologies.
The branch of Carbon Capture and Sequestration (CCS) offers medium-term solutions for matching the transition to an economy based on renewable sources with the current energy mix, mostly based on the generation of power, cement and other commodities from fossil fuels. Considering that anthropogenic emissions of CO_2 from fossil fuel combustion and industrial processes contributed about 78% of global GHG emissions increase from 1970 to 2010, the impact of these systems on the GHG reduction is extremely determinant.
The technical and motivational issues associated to the CCS sector represent also the background of this PhD thesis, focused on the numerical simulation and techno-economic analysis of advanced technologies applied to cement plants for reducing CO_2 emissions and for generating CO_2–free electricity. Cement industry, whose manufacturing process is extremely energy demanding and CO_2 emitting, will likely be affected by the new environmental legislations even more than power plants. Cement industry can count on a global production capacity of about 5.5 billions of tons per year, distributed worldwide over more than 5700 facilities that are responsible for the 7% of CO_2 emitted from stationary sources. The total volume of concrete consumed by society worldwide is second only to water: clinker is a vital construction material and a strategic commodity, especially for developing countries. In the present and future industrial scenarios, the global steep rise of cement production is necessary for simplifying the shift to a green economy, involving the construction of renewable energy facilities and new infrastructures. Cement production is based on an energy intensive process: it requires thermal power for the progressive heating of a raw meal to the kiln temperature (1450°C) and for sustaining the chemical processes that govern the clinker formation. The most energy demanding process is the endothermic limestone calcination ($CaCO_3$|$CaO+CO_2$ @850-900°C), sustained by fuel combustion in a proper reactor (calciner); a second combustion is then necessary within the rotary kiln, where the calcined stream (CaO, SiO_2, Fe_2O_3 and other minerals) reaches its peak temperature and start reacting to form the clinker constituents. Hence, CO_2 is released from both fuel combustion and $CaCO_3$ decomposition: unlike the CO_2 emitted by many industrial processes, two-thirds of cement plant emissions are generated by chemical processes, whereas only one-third comes from fuel combustion. Exhaust gas leaves cement plant with a CO_2 concentration higher than 30% (resulting in 900 kg_{CO2}/ton_{Cem}). Several actions are practicable for reducing these emission below the levels suggested by recent roadmaps (fuel substitution, alternative cements, energy efficiency), but in all the scenarios the role of CCS is essential for achieving the 2050 targets on CO_2 emission reduction suggested by EU. Without CCS, the application of the greenest technology could be suffice to avoid only a small fraction of the CO_2 currently emitted by the process: a full substitution with renewable energy sources would not solve the problem of the inherent emission associated to limestone calcination, which amounts to the 60% of the total CO_2 released by the cement plant. This study aims at characterizing two novel CCS concepts belonging to the family of advanced post-combustion capture methods: Calcium Looping (CaL) and molten carbonate fuel cells (MCFC). CaL process exploits the capability of CaO to react with CO_2 (contained in some combustion exhausts) forming $CaCO_3$ by means of a relatively high temperature (650°C) exothermic reaction occurring in a CFB reactor (carbonator); here, reaction heat can be efficiently recovered for steam and electricity production. In the following step, the reaction product ($CaCO_3$) is regenerated in a second oxy-fuel reactor (calciner), which promotes the calcination in a CO_2-rich atmosphere. The resulting CO_2 flux is cooled, compressed and stored, while the regenerated sorbent (CaO) can be recycled again to the calciner for the next capture cycle. Originally ideated for power plant applications, CaL technology is progressively reaching high Technology Readiness Levels (TLR), thanks to the global R&D interest generated by successful results demonstrated in medium scale pilots. Two different Cal processes are studied in this work (indirect/direct): the first relies on the possibility of using calcium species purged from a CaL power plant as raw meal for a cement plant, substituting in this way the conventional solid feed coming from the cave with a pre-calcined material. The Cal application in a power plant requires a continue solid purge from the calciner for extracting ash and sulfur species introduced with coal in the reactors loop. The solid purge is mainly constituted by CaO, previously defined as the main species participating to the clinker formation and to the cement plant CO_2 emission/fuel consumption. If the conventional cement plant raw meal was substituted by the purge coming from the Cal power plant, the overall CO_2 emission and the primary energy consumption associated to calcination would reduce drastically. This study will show that the overall fuel consumption within the cement plant can be reduced of about 60-70%, while the CO_2 avoided can reach even higher values. The main issues related to this synergy process are investigated in detail: in order to match properly the cement plant size with the mass flow rate of solid purged from the power plant (and used as raw meal), a big size CaL power plant (500-800 MW_{el}) must be considered, and depending from CaL operating parameters, different level of integration will be feasible. Indeed, the solid purge is composed not only by CaO but also by ash and sulfur compounds. Since amount of side-species fed to the cement plant must respect the very strict ranges related to the cement composition, the purity of the CaL purge defines the maximum integration level between the power and the cement plants, as well as the overall material, energy and emission savings.
The second application (direct CaL process) requires a substantial retrofit of the cement plant calciner, which must be converted to an oxyfuel operation. The concept consists is recycling part of the calcined material to an entrained flow carbonator: this CaO stream is then used as a sorbent for capturing CO_2 from the exhaust gases leaving the rotary kiln. In this way, gaseous effluent leave the cement plant with a minor CO_2 concentration, whereas the reacted sorbent ($CaCO_3$) can be recycled to the cement plant calciner, where it is converted to CaO for starting a new capture cycle; thus, the cement plant calciner plays the double role of sustaining the CaL process and the of feeding the rotary kiln. CO_2 leaving the calciner can be cooled (producing steam and power), compressed and stored. The last process here simulated regards the utilization of Molten Carbonate Fuel Cells as CO_2 concentrators and electricity generators in cement plants, and has been simulated with the support of an experimental activity. The concept of using MCFC as CO_2 concentrations relies on the necessity of feeding the cathode of these devices with a CO_2-rich stream: the idea

consists in feeding MCFC modules with cement plant gaseous exhausts, exploiting their high CO_2 concentration for obtaining a high MCFC power density and an excellent energy conversion efficiency. The catalytic reaction occurring at the cathode side involves the formation of $CO_3^=$ ions starting from O_2 and CO_2. The carbonate ions produced on the nickel surface of the cathode pass through a selective membrane, where the electrolyte promotes their migration to the anode; here, these ions react with H_2, producing H_2O and CO_2. For each $CO_3^=$ ion transferred through the fuel cell membrane, two electrons flows via an external circuit, generating a current flow. The stream leaving the device at the cathode side is hence purified from a certain amount of CO_2, which is concentrated in the other gaseous effluent exiting the anode side. The latest is also composed by H_2O and unconverted syngas, and can be further processed before being compressed and stored. The MCFC working temperatures (650°C) and the nickel surfaces allow to feed the anode with natural gas, which is internally reformed exploiting the waste heat released by the electrochemical process and the progressive H_2 consumption. Several issue must be faced for studying the feasibility of this application. First, cement plant exhausts contains dangerous traces of some substances that could poison fuel cell materials: deep gas clean-up systems must be considered. Second, one of the fuel cell disadvantages is the difficulty in reaching high CO_2 separations, because the lower the reactant partial pressure, the higher the diffusion resistance, that eventually lead to large efficiency penalties. This and many other issues have been evaluated to find out the best configuration in terms of carbon capture rate and net electric efficiency.

All the proposed applications overcomes the 80% of CO_2 capture efficiency; their economic competitiveness is also confirmed in the final section of the thesis, through a set of techno-economic sensitivity analysis. The whole work has been sustained by the competence and the resources of two companies strongly involved in these sectors, namely Italcementi Spa and Fuel Cell Energy Inc., and is based on detailed simulations (GS/Aspen plus) of cement and power plants accurately calibrated against real plant performances. Specific models have been created in Matlab and Fortran codes for the simulation of chemical reactors and fuel cell modules, that represent the technological core of these CO_2 capture processes.

HIGH FIDELITY 1D MODEL FOR SELECTIVE MEMBRANE SIMULATION IN CCS POWER PLANTS

Ing. Davide Maria Turi - Supervisors: Prof. Ennio Macchi, Prof. Paolo Chiesa

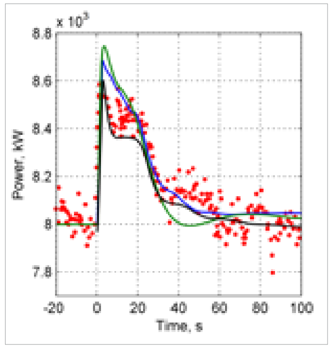
During the last two centuries, the concentration of carbon dioxide in atmosphere increased approximately from 275 to 400 ppm. This higher concentration has already produced effects on climate, accordingly to indications of most of climatic models; this trend will dramatically change the global temperature in the next decades. The control of the anthropogenic greenhouse gas emissions is one of the most important challenges for the next years. Energy production from fossil fuel is responsible of a great part of the greenhouse emissions. In the last ten years, has been much effort on finding a long term solution to this problem, mostly based on innovative and clean power technologies. Even if renewable sources of energy could cover part of the energy demand, the world is likely to remain fossil fuel dependent. In order to reduce greenhouse gas emissions while continuing to use these fuel to satisfy a significant fraction of our energy demand, different technologies to capture CO_2 are under investigation. One way to reduce CO_2 emissions in atmosphere from fossil fuels is Carbon Capture and Storage (CCS). In this field, in the latest years different innovative technologies for near-zero emissions plants have been investigated. Carbon capture processes in a coal or natural gas power plants, falls in one of the following three main categories: Pre-combustion where CO_2 separation occurs from synthesis gas, downstream a water gas shift reactor, Oxy-combustion where the energy conversion process is modified (typically by using oxygen as comburent agent) and CO2 separation from flue gases (post-combustion). A new advanced technology, based on the selective membranes could be applied in all the three different categories. In this thesis a detailed model for the simulation of the membrane reactor was developed, then used for the investigation of selective membranes in coal and natural gas feeding power plants. There are several categories of membranes; in this thesis, three of those has been assessed, selective to H_2, O_2 and CO_2. The first one used in pre-combustion systems, due to its positive effect on reforming and water gas shift reactions. By extracting hydrogen from the reacting syngas stream, the charge conversion is favored leading to significant efficiency advantages. Oxygen membranes could be used in pre-combustion and Oxy combustion plants, in substitution of the ASU (Air Separation Unit), for the production of a stream of pure oxygen. CO_2 membrane could be a good alternative to chemical solvents in post combustion power plant, reducing the efficiency penalty and environmental issues related to amines. This work presents a model for the integration of membrane modules in energy conversion systems, involving three equations for the mass flux across membrane surface: (i) Wagner's equation for dense perovskite membranes, (ii) Sievert Law for palladium membranes, (iii) Solution diffusion equation for CO_2 membranes. The great flexibility of Aspen Custom Modeler, together with a good implementation of the code permit to simulate different types of membranes by the integration of proper permeation equations. In case of oxygen flux, the model is based on accurate experimental measurements and incorporates the effects of chemistry at the surface and diffusion in the bulk, as well as heat and mass transport on the feed-side and sweep-side. A code validation was obtained starting from several data present in literature or derived from European projects. The simulation has been performed for Oxygen, Hydrogen and Carbon dioxide membranes. The first two technologies integrated in IGCC systems and the last one in NGCC power plants. One of the most promising application of the membrane technology is oxy-combustion; the use of high temperature ion transport membranes can substitute air separation units, by the integration of the membrane reactor in the gas turbine. In ICOT configuration most of theoxygen is produced in anOTMinstead of a cryogenic ASU. Oxygen isr emoved from the high-pressure airstream exiting the gas turbine compressor. Since oxygen transport membrane requires elevated temperature to ensure adequate permeation, the airstream is heated by partially burning the syngas. A small cryogenic ASU is present in the plant to producethe nitrogen needed in the lock-hoppers for coal loading intothegasifier and the cleaning of the candle filters. The net electric efficiency rise form 35,3 (reference case) to 37,9% (LHV). Pd-based H2-selective membranes can be also integrated in the gasification island for the separation of a hydrogen from syngas. After a preliminary assessment, both technic and economic analyses are considered. Membrane separation section is basedon several membrane modules in series, with a diabatic high temperature shift in between. Following the results of previous works there are two different layouts that can be assumed.The first configuration where all the hydrogen permeates at high pressure and feeds the gas turbine.This layout achieves very high net electric efficiency (about 40%), but requires large membrane surface area with penalties from economic point of view.In the second configuration, part of the hydrogen is separated at low pressure and used for post firing applications. This configuration preserves the efficiency of the previous case but reduces significantly the membrane surface area. In this thesis, the second layout is reported, making the results consistent with the application reported above. In the last part of the thesis, CO_2 membranes are investigated. This technology can be used in coal or natural gas feeding power plants. A techno-economic analysis of NGCC integration has been assessed. Such a configuration is based on a"two-step" system; the first one separating CO_2 for sequestration, the second one used to generate a selective CO_2-rich flue gas recycle. Three different technology has been investigated; DOE, Huang and Polaris membranes, applying a combination of those in order to maximize the efficiency and reduce the CO_2 avoided cost. Due to the use of a combined configuration with DOE and Huang membranes a total cost of 87US$/t CO_2 is obtained, providing a competitive alternative to MEA absorption (83€/tCO_2). On the contrary this CCS technology imply an increase of the LCOE, which passes from 60 to 87 €/MWh, suggesting that further improvement are needed, extending membrane life and cost reduction.The economic assessment is based on the methodology proposed by EBTF. This methodologyneglects transport and storage costs; at considered plant sizes they are modest and, most of all, not related to the capture technique. Reference costs for transport and storage are in the range of 1-4 $/t$CO_2$ and 6-13 $/t$CO_2$, respectively. The variation depends on power plant distance from the storage site and the type of storage assumed. The cost of electricity is calculated from adopted IEA models by setting the net present value (NPV) of the power plant to zero. This can be achieved by varying the plant COE until the revenues balance the cost over the whole lifetime of the power plant. Labor costs refer to an average European social environment. For maintenance and insurance costs, the approach was taken from IEA and coefficients were corrected according to EBTF figures. Total plant costs are calculated with the Bottom-Up Approach (BUA). This approach is the most typical for innovative plant where no construction experience exists. The first step consists of calculating Total Direct Plant Cost from equipment costs and then adding installation costs such as piping, erection, Outside Battery Limits, etc. Total direct plant costs plus indirect costs, which are calculated as a percentage of direct plant costs, lead to Engineering, Procurement and Construction costs. Finally, Total Plant Cost results from EPC plus owner's cost and contingencies.

DEVELOPMENT OF NEW TOOLS FOR THE ANALYSIS AND SIMULATION OF CIRCULATING-FUEL REACTOR POWER PLANTS

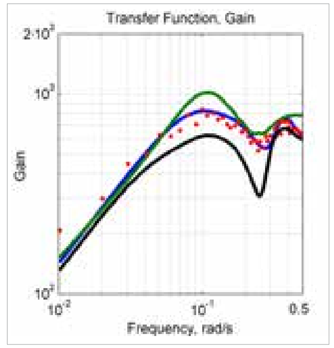
Matteo Zanetti - Advisors: Prof. Antonio Cammi, Prof. Lelio Luzzi

The context of the thesis is the research domain oriented towards the development and assessment of advanced simulation tools to study the dynamics of circulating-fuel nuclear reactor plants, represented by Molten Salt Reactors (MSRs).

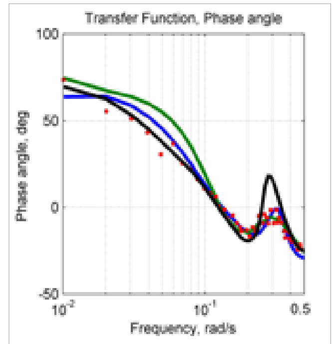
New and reliable tools are required by the particular nature of MSRs, in which a single fluid acts both as fuel and coolant. This double role gives rise to peculiar phenomena, such as:
i) drift, redistribution and out-of-core decay of the Delayed Neutron Precursors (DNP), that reduce the prompt criticality margin due to the loss of a fraction of the delayed neutrons available for the chain reaction;
ii) heat transfer involving direct heat production in the fluid.
These aspects lead to a complex and highly coupled physical environment that cannot be addressed using modelling approaches and codes developed for solid-fuelled nuclear reactors, without major modifications of their basic structure.
In the recent years, several modelling approaches for MSRs have been proposed with different aims. We can identify: validation of models, investigation of reactor characteristics, design studies, safety studies, and finally control-oriented studies. In this vast field of researches, only few studies for modelling a whole MSR system are present. Interestingly, the efforts of most of the institutions involved in MSR research have converged to simulate the core in a Multi-Physics (MP) framework. In this case, the Multi-Physics Modelling (MPM) approach is the state-of-the-art for simulating the behaviour of MSR cores. It is based on the node-wise and time step-wise coupled solution of the Partial Differential Equations that describe the modelled phenomena. That approach is excessively computational heavy for the simulation of whole nuclear reactor plants, but it can be adopted for studying in detail single plant components (e.g., the core).
This thesis tries to answer the lack of modelling options dedicated to the simulation of MSR plants. A first tool has been obtained from the extension of a current state-of-the-art system code (i.e., NRC TRACE). An innovative tool, that represents an evolution of the first one, has been then developed. This tool, based on the Geometric Multi-Scale approach, was conceived to use MPM as a key part and allowed to investigate the pros and cons of using innovative or traditional approaches.
The verification of these new simulation tools has been provided by building models that take into account the principal characteristics of MSRs, with a focus on control-oriented features. In particular, the relation between integral quantities, such as power, temperature and mass flow rate, has been determined by means of the evaluation of transfer functions. The results provided by the models have been compared with appropriate references.
Modelling activities have been focused on two MSR designs: the Molten Salt Reactor Experiment (MSRE) and the Molten Salt Fast Reactor (MSFR). In this way, both thermal (graphite-moderated), and fast spectrum options have been considered. The MSRE plant, built at Oak Ridge National Laboratory (ORNL) in the 1965, is fully characterized and experimental data from reactor operation are available. The MSRE consisted in a core in which the fuel flowed through a number of graphite channels and a single cooling loop. An intermediate loop provides for separation of the fuel system from the final heat sink. Available transient experimental data and experimentally determined transfer functions have been used as reference. The MSFR is under development in the frame of series of EURATOM Projects (see http://samofar.eu/). It is constituted by a homogeneous channel-free core. Sixteen loops provide for cooling capabilities, with an intermediate circuit envisaged to segregate the fuel from the energy conversion system. A MPM-based model developed at PoliMI Nuclear Reactor Group was taken as reference.
The endeavours of the thesis followed two main directions:
i) The US Nuclear Regulatory Commission system code TRACE has been extended to MSRs, providing it with capabilities to simulate MSR materials, the behaviour of DNPs and decay heat generation in circulating nuclear fuel. The extended code has been used to simulate both the MSRE and the MSFR.
ii) A new tool based on the Geometric Multi-Scale (GMS) approach has been developed, which is aimed at the integration of traditional control-oriented models and/or system codes with MPM-based components. The GMS approach consists in identifying a geometrical hierarchy among the different components of a system and modelling them accordingly, ranging from 3D to 0D description. Here, the choice of the dimensional representation of a component is also based on the expected importance for the whole system dynamics or to add better modelling capabilities for some physical phenomena. From a different perspective, the GMS approach can be recognized as a means to build comprehensive MP models with reduced complexity, developing appropriate connections among its different parts and handling the boundary conditions with low dimensional models.
The GMS approach has been used to model the MSRE, connecting 3D MPM-based models of core channels to a collection of 0D components that describe the power conversion system.
Comparison with experimental data has shown satisfactory predicting capabilities of the developed simulation tools. To understand the improvements brought by the use of the GMS approach in MSR modelling, the MSRE behaviour at nominal power has been considered. Results from simulations were analysed both in the time and frequency domains. In Figures 1-3, it is shown how the increase in modelling complexity and computational burden improves the fidelity of the simulation to the experiment. The different options for MSR plant modelling made available by means of this work can be selected according to the required accuracy and needs for the system under analysis.



1. MSRE response to a 13 pcm reactivity insertion at full power. In black: ORNL 0D model; green: extended TRACE; blue: GMS; red dots: experimental data.



2. MSRE power to reactivity transfer function, gain. In black: ORNL 0D model; green: extended TRACE; blue: GMS; red dots: experimental data.



3. MSRE power to reactivity transfer function, phase angle. In black: ORNL 0D model; green: extended TRACE; blue: GMS; red dots: experimental data.