Publishable Summary

- Project Context and Objectives

The overall concept of the AMCOS project is the study of the prospect of newly synthesized materials by the Indian institutions to be used as capturers of carbon dioxide and methane. The means towards this task are various computer experiments, namely, first principles *ab initio* calculations, and classical statistical mechanics based molecular simulations, such as Molecular Dynamics and Monte Carlo, as well as conventional *ad hoc* designed experiments so that to be directly comparable to the mentioned above molecular simulation computer experiments. Moreover, in addition to the tasks of the AMCOS project, though within its context, taking advantage of the experimental techniques developed during the entire period, the dynamics of hydrogen as a sorbate molecule in these materials was also investigated.

Over the past decade a branch of organic synthesis following a reticular process, gave a vast rise to oriented design and production of new materials characterised by exceptional physicochemical properties. This strategy of synthesis engineering towards target structures, created a novel class of advanced sorbents such as the zeolitic imidazolate frameworks (ZIF), characterized by large pore sizes, high apparent surface areas and a chemically active interior. In addition, selective modification of polymeric matrices has led to the so-called functionalized polymers (FP) which exhibit improved performance futures, for instance, the enhanced ability for adsorbing specific group of molecules. Also, functionalization processes of porous silicas by aminopolymers of low molecular weight, have developed a new category of inorganic-organic hybrid sorbents, the hyperbranched aminosilicas (HAS).

Objective of the AMCOS EU-India collaborative research project is to investigate the capability of newly synthesized or/and modified classes of the aforementioned advanced materials, for use in environmental applications such as the selective separations of carbon dioxide in flue gases and natural gas. For this purpose, the sorbate molecular dynamics and thermodynamics will be studied extensively by applying, developing and integrating state-of-the-art computational tools and experimental methodologies.

The task of **NTUA** under AMCOS is the statistical mechanics based modeling of the sorption thermodynamics and kinetics of various molecules in recently synthesized ZIF structures in order to investigate the evolution of the sorption equilibrium over a wide range of occupancies of carbon dioxide, and to elucidate its rate and mechanism of motion in the pores of these materials. During the current reporting period NTUA examined the ZIF-3 and ZIF-8 as representative members of the series of ZIF structures.

The simulation predictions will be then compared with the measurements of the **IRCE-LYON** group which is responsible for measuring the guests' mobility via Quasi-elastic Neutron Scattering experiments (QENS). Simulation and QENS, both being microscopic techniques, can provide valuable information on the sorbate molecular dynamics in the ZIFs.

UNISS has developed an easy procedural protocol to derive partial charges on ZIFs from DFT-based quantum chemical calculations. The chosen structure to test was also ZIF-3 and ZIF-8, both widely studied through physical experiments. To obtain more reliable charges, several DFT calculations on a periodic ZIF-8 were carried and crosschecked one with each other and with cluster-based DFT calculations on ZIF-8 fragments of increasing size. In quantum chemical calculations for non-periodic system GAUSSIAN, TURBOMOLE were used, whereas CPMD and cp2k packages were used for periodic systems. Both the periodic ZIF-8 lattice and its various fragments have been digitally reconstructed from the X-ray crystal data collected from the Cambridge Crystallographic Data Centre (CCDC) [www.ccdc.cam.ac.uk]. For periodic DFT calculations, the fitting of the quantum chemical electrostatic potential to atomic site charges is performed with the REPEAT (Repeating Electrostatic Potential Extracted Atomic) method, whereas the CHELPG and MK scheme were used for DFT calculations on fragments.

The task of **LU** is to provide experimental data on diffusion of adsorbate molecules in the advanced adsorbent materials. These experimental data are required to validate the corresponding computational studies of the Indian and European AMCOS partners. The adsorbent materials considered during the report period are the MOF CuBTC as test material and crystalline ZIFs. The nanoporous amorphous HAS and polymer based adsorbents were not yet been synthesized by the Indian project partners. Due to the main target of the project, which is the exploration of these materials for their suitability for CO_2 separation from gas mixtures, the focus in the first report period was to study single component diffusion of carbon dioxide and alkanes (methane, ethane) in selected materials. For the purpose of the CO_2 diffusion studies, the ^{13}C pulsed field gradient (PFG) NMR technique needed to be developed which included NMR probe design and development of measurement protocols. Simultaneously to our efforts to improve and establish ^{13}C PFG NMR diffusion studies with adsorbed carbon dioxide in MOF's and ZIFs LU possesses the opportunity to measure transient concentration profiles during uptake and desorption of guest molecules in adsorbent particles by infrared (IR) microscopy. During the report period, such diffusion measurements were successfully carried out with ZIF-8 as adsorbent and carbon dioxide and methane as well as with mixtures of both molecules as adsorbate gases.

Computer modeling and screening were performed on materials synthesized by the Indian consortium. In particular the EU consortium worked on selected materials from the Zeolitic Imidazolate Framework homologue series and from Functionalized Polymers.

The basic axis of the employed methods for the analysis of the efficiency of the provided materials in capturing the guest sorbates is the computational modeling utilizing Quantum mechanical calculations and also statistical mechanics based mesoscopic and atomistic simulations of the sorption processes. Nevertheless, the phenomena pertaining to sorption in a real process is much more complicated as adsorption on the surfaces, penetration in the interior of the materials (diffusion) along with inter-crystalline transport occurring fast or infrequently depending on the energetics of the system sorbent material / guest sorbate. That led us to develop not only methodology toward the study of the thermodynamical phase equilibrium, but also study of the kinetics of the guest system within the host material as well.

The novelty of the materials of the project and consequently the complete lack of a force field (FF) imposed a strategy in two directions towards a) creating of reasonable FFs on a Quantum Mechanical basis, and b) adopting sophisticated "expensive" experiments measuring the aforementioned kinetic and dynamics information under comparable time and length scales, so that one to be able to compare the results obtained from the computer simulation experiments.

The principle sorbate of the work during the entire period was the Carbon Dioxide (CO_2), and the central objective was the investigation of the aforementioned sorbents' performance in capturing the CO_2 molecule, and also, by modeling the physicochemical processes involved for this, to explain and predict the impact of the materials' structure on the CO_2 storage efficiency. In addition to this, it proved imperative the inclusion of Methane (CH_4) and Hydrogen (H_2) in the original target sorbates as well. The reasons for this are: (i) In almost all applications CO_2 coexists with at least one of the above molecules; (ii) CH_4 remains a potential threat to the environment especially in view of the increasing melting of the earth's ice-lands; (iii) H_2 is still a promising green fuel, and, (iv) in many cases from the perspective of both the computer modeling and screening, it was particularly useful from methodological issues to use the later sorbents as probe means before CO_2.

- Work Performed

ZIF-8 and ZIF-3 crystals were modelled using rigid, and at the end of the project, flexible force fields. The rigid model keeps the crystal atoms fixed at their positions, identified by XRD data. Therefore, structural characteristics remain unaltered throughout the simulations. The crystal atoms interact with sorbates through both long and short range forces. We tested both the Dreiding and the Universal Force-Field (UFF) dispersion interactions parameters. Two flexible models were tested for ZIF-8 and ZIF-3. The crystal atoms are allowed to move in molecular dynamics simulations of bare frameworks. Both flexible models include bond stretches, angle bends, inversions (improper torsions), dispersion and electrostatic interactions. The Dreiding and Nilsson parameterizations were used. For the electrostatic interactions, the same charges were used as in the rigid model. It must be also noted that the quantum mechanical calculations have given the modeling a new input for the Molecular Dynamics simulations applied to the flexible models of the metallorganic frameworks of the project. The temperature was chosen to be 258 K, according to the XRD experimental data found elsewhere. Bond lengths, angle bend, improper and proper torsion angle values were computed as statistical averages throughout the runs of 100 ns. The obtained results showed excellent agreement with experimental values. Simulations were also carried out at a lower temperature to investigate the effect of temperature on the structural conformations for both ZIF-3.and ZIF-8 structures.After the first successful 13C and 1H PFG NMR diffusion studies of the adsorbed CO_2 and CH_4 in the nanoporous MOF CuBTC, which were performed in order to check the developed pulse field gradient NMR probe, it was the next task to perform these NMR diffusion measurements on the Zeolitic Imidazolate Framework ZIF-8. The previous NMR investigations were performed at gas phase pressures below 1 bar. They showed that the adsorbed amount of CO_2 and CH_4 in ZIF-8 is substantially smaller than in CuBTC which rendered NMR diffusion studies impossible [1]. Therefore, it was decided to explore the possibilities to perform NMR diffusion studies at elevated gas pressures. The target of 10 bar for these measurements was discussed among the AMCOS project partners. LU extend the experimental equipment for the NMR studies accordingly enabling NMR measurements at up to 15 bar. Methane and Carbon Dioxide NMR measurements have been accomplished in ZIF-8 using this new high-pressure NMR set up.. The NMR data for the relaxation times showed that the gases are in the adsorbed state. The obtained self-diffusion coefficients are in the same order of magnitude than previously published data of IR microscopy but point towards a different loading dependence. Especially for the carbon dioxide in ZIF-8, a good agreement between the NMR experimental results and results of MD simulation provided by UNISS and NTUA were found. This points towards a successful approach and development of the computational tools developed within AMCOS. PFG NMR studies of CH_4 / CO_2 self-diffusion in mixtures were also performed, and show that there seems to be only a minor effect on the mobility of one species in the presence of the other species. Comparisons are now being made between the experimental and computational methods on these adsorbed binary mixture.

In situ quasi-elastic neutron scattering (QENS) experiments were performed at the Institut Laue-Langevin, in Grenoble, France, on H_2, CH_4 and CO_2 in the two samples provided by NEERI : ZIF-8 and ZIF-3, where the linkers were deuterated. From the variation of the broadening as a function of wavevector transfer, diffusion coefficients could be derived at three different H2 concentrations. Although the quality of the spectra recorded for CO_2 was not optimal, diffusivities could be extracted at 200 K, at four different loadings. The statistics obtained for CH_4 were better because of the larger incoherent cross section of this molecule. Comparisons are now being made between the different methods.

- Results

Statistical mechanics based simulation studies at the atomistic level of Ar, CH_4, D_2 and H_2 sorbed in the ZIF-8 and ZIF-3 were accomplished. So far we have explored the mechanisms that govern the sorption thermodynamics and kinetics of non polar sorbates possessing different sizes and strength of interactions with the metal-organic framework, in order to understand the outstanding properties of this novel class of sorbents, as revealed by experiments published elsewhere. For this purpose we developed in-house modeling procedures involving calculations of sorption isotherms, partial internal energies, chemical potential in the fully flexible host structure various probability density functions and molecular dynamics, for the modeling of sorbed phase over a wide range of occupancies inside a digitally reconstructed unit cell of ZIF-8. The results showed a marked energetic inhomogeneity perceived by the sorbates as a consequence of the 2-methylimidazolate links in the atomic framework of the metal-organic material under study, resulting in free energy barriers which give rise to inflections in the isotherms and guide the dynamics of guest molecules.

Single component CO_2 NMR studies were performed with Imidazole Functionalized Polystyrene (Im-PS) obtained from ICT Mumbai. ^{13}C NMR spectroscopy confirmed that the CO_2 is rather strongly interacting with the imidazole functional group in this polymer. In agreement with this spectroscopic characterization, ^{13}C PFG NMR diffusion measurements at elevated gas pressure of 10 bar showed that in the adsorbed carbon dioxide has short transverse relaxation times rendering intraparticle self-diffusion studies in these f-PS samples impossible. The NMR diffusion studies yield only the long-range mobility between individual adsorbent particles via the gas phase.

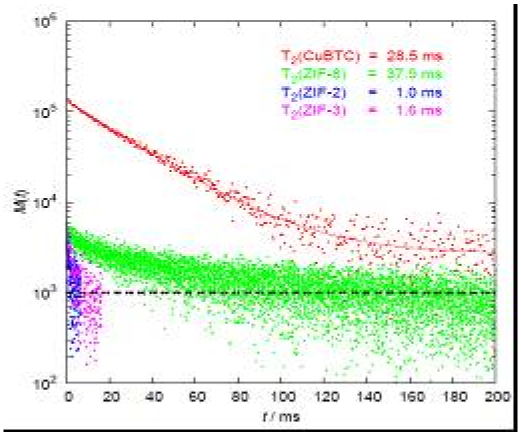

Fig. 1 Initial NMR signal intensity and transverse magnetization decay M(t) of $^{13}CO_2$ in ZIF-8 (green), ZIF-2 (blue) and ZIF-3 (purple) compared to CuBTC (red) measured the CPMG NMR sequence; the averaged r.m.s. noise level in these measurements is indicated by the black dotted line

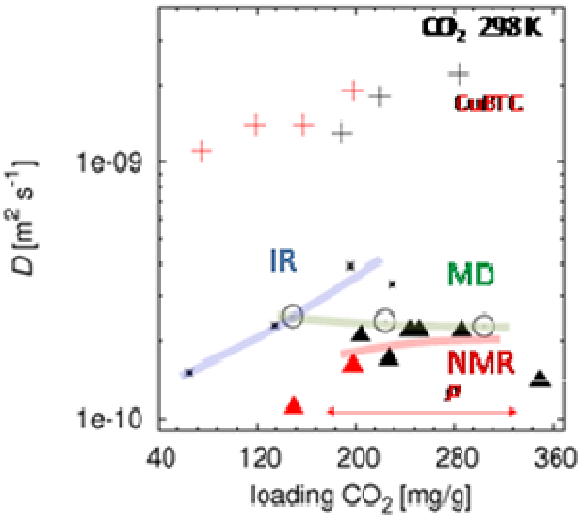

Fig. 2 Carbon dioxide self-diffusion coefficient in ZIF-8 in the binary mixture (▲) with methane and as single component (▲) measured by ^{13}C PFG NMR at 298 K. The NMR data are plotted as function of CO_2 loading. For comparison, data from IRM (black stars, H. Bux et. al [Adv. Mater. 22, 4741-4743 (2010)]) and MD simulations (open bullets) as well as for CuBTC (crosses) are given.

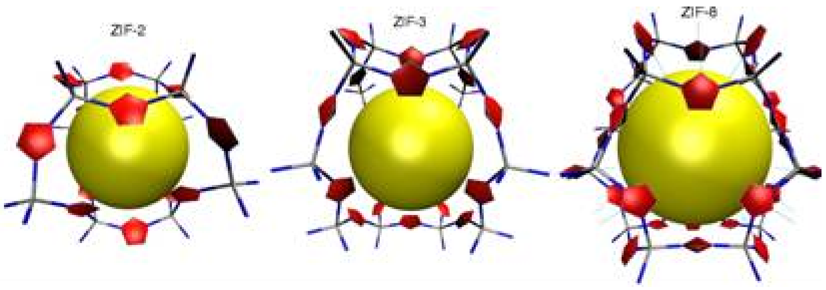

Fig. 3 Crystalline geometries of ZIF-2, ZIF-3, and ZIF-8 with large cages shown by yellow spheres of diameter 6.00 Å, 8.02 Å, and 11.60 Å (given for experimental structures), respectively. Repeating square-hexagonal, square-octagonal, and square-hexagonal small cage sites are well exposed in the given modeled structures for ZIF-2, ZIF-3, and ZIF-8. Coordinating Zn centers are shown by gray color and ligating N centers by blue color. The dangling bonds stand for the extension of the patterned structure. -CH3 groups in ZIF-8 is shown by green stick. H atoms are omitted for clarity.

During the second period of the project is presented a detailed picture of the distribution of charge density across functionalized and non-functionalized frameworks via determination of electrical dipole moment separately at metal and ligand sites. The values of dipole moments were calculated from the analysis of maximally localized Wannier function and ion centers, and from corresponding charges. Based on our dipole moment analysis we rationalized the sorption of CO_2

in these materials by combined Monte Carlo simulations. The adsorption thermodynamics and the uptakes of CO_2 at the low pressure range depend on the strength of solid-gas interaction, increasing in accordance to the trend of the dipole moment, in the order ZIF-3 > ZIF-2 > ZIF-8. Moreover, the location and magnitude of the dipole moment vectors across the framework are important for identifying correctly the preferred adsorption site for CO_2 near the frameworks. Some other properties of these materials like mechanical and chemical stabilities can also be addressed through the knowledge of these dipole moments calculations.

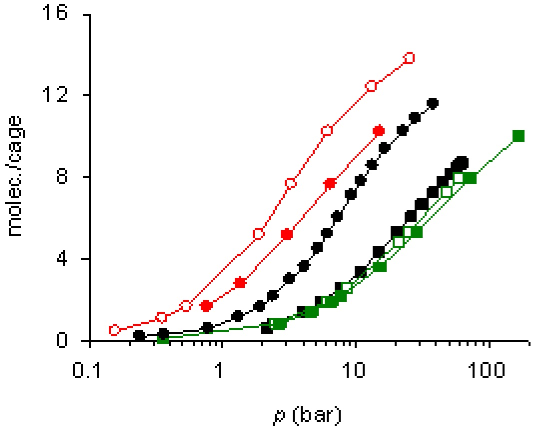

Fig. 4 Isotherms computed via Molecular Dynamics for CH_4 at 300 K (green squares) and CO_2 at 303 K (red circles) in ZIF-8, versus measurements of CH_4 at 300 K,[13] and CO_2 at 303 K,[14] (similar symbols in black); simulations are conducted under isochoric-isothermal (open symbols) and isobaric-isothermal ensembles (filled symbols).

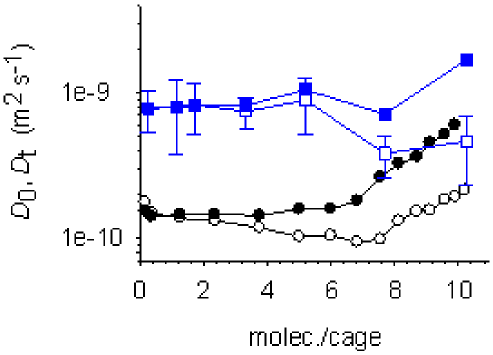

Fig. 5 Predicted collective diffusivities (blue squares) of CO_2 as a function of loading, in a flexible ZIF-8 model with its bridging ligand group (2-methylimidazolate) capable of quasi-free motion versus IRM measurements.

- **Impact of the Results**

Through the computational work it was revealed the influence of the mobility of the sorbent framework on both the equilibrium and kinetic properties of the sorbed phase by means of Molecular Dynamics computer experiments, under both isochoric- isothermal and isobaric-isothermal statistical ensembles, for several host model options, combined by Widom averaging along the entire trajectory of the host-guest system toward rigorously obtained sorbate isotherms within a fully flexible lattice. This novel methodology was adapted to the study of the Self-diffusivity and the collective (Maxwell-Stefan and Transport) diffusivities of Carbon Dioxide and Methane within the Zeolite Imidazolate Framework-8. The simulation predictions are compared with measurements from Pulsed-Field Gradient Nuclear Magnetic Resonance (PFG NMR), as well as with recently conducted Infrared Microscopy (IRM) experiments elaborated on the basis of the current modeling in the flexible ZIF-8. The modeling results predict a significant influence on the sorbate transport, exerted by the 2-methilimidazolate ligands surrounding the cage-to-cage entrances, whose apertures are commensurate with the guest molecular dimensions. Moreover, calculations of the singlet probability density distribution (Fig. 6) of the sorbate molecules at selected regions within the imidazolate framework provide a plausible explanation of the transport diffusivity as a function of sorbate occupancy, measured via IRM.

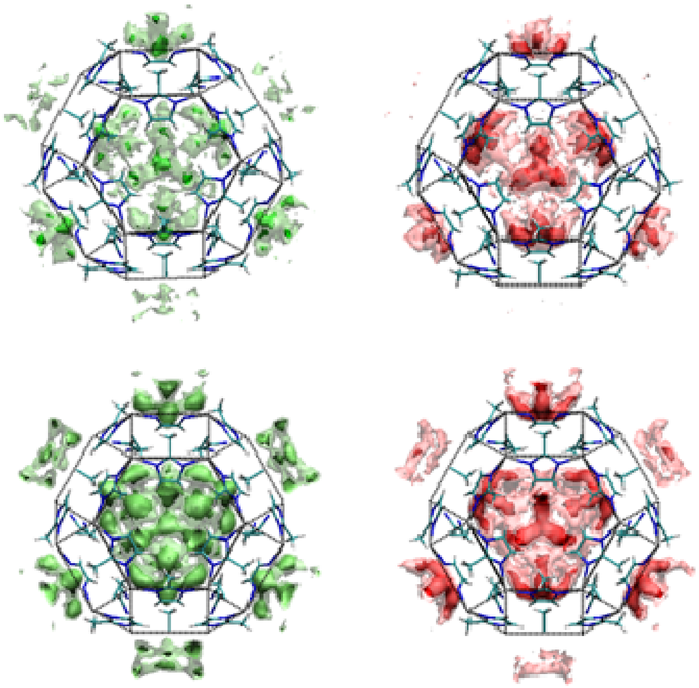

Fig. 6. Top: Isodensity surfaces calculated in the vicinity of the hexagonal windows of ZIF-8 for CH_4 (left), and CO_2 (right), at low pressures; bottom: same as above for high pressures. Low to high density values follow the color code light to dark respectively.