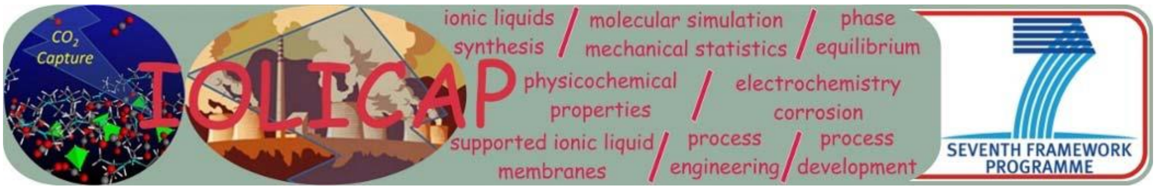

IOLICAP – Novel IOnic LIquid and supported ionic liquid solvents for reversible CAPture of CO_2

Project number: 283077
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Project Final Report

February 2016

PROJECT FINAL REPORT

Grant Agreement number: 283077
Project acronym: iolicap
Project title: Novel IOnic LIquid and supported ionic liquid solvents for reversible CAPture of CO_2
Funding Scheme: FP7-ENERGY-2011-1

Date of latest version of Annex I against which the assessment will be made:

Periodic report: 1st ☐ 2nd ☐ √ 3rd √ 4th ☐
Period covered: from 01/12/2014 to 29/02/2016
Name, title and organisation of the scientific representative of the project's coordinator[1]:

Dr. George Romanos
N.C.S.R. Demokritos
Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems
Terma Patriarchou Gregoriou & Neapoleos str.,
Aghia Paraskevi Attikis, 15310
Athens, Greece

Tel: +30-210-6503972
Fax: +302106511766
E-mail: g.romanos@inn.demokritos.gr

Project website[2] address: http://www.iolicap.eu/

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[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

[2] The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.

Declaration by the scientific representative of the project coordinator

I, as scientific representative of the coordinator of this project and in line with the obligations as stated in Article II.2.3 of the Grant Agreement declare that:

- The attached periodic report represents an accurate description of the work carried out in this project for this reporting period;
- The project (tick as appropriate) [3]:
  - √ has fully achieved its objectives and technical goals for the period;
  - ☐ has achieved most of its objectives and technical goals for the period with relatively minor deviations.
  - ☐ has failed to achieve critical objectives and/or is not at all on schedule.
- The public website, if applicable
  - √ is up to date
  - ☐ is not up to date
- To my best knowledge, the financial statements which are being submitted as part of this report are in line with the actual work carried out and are consistent with the report on the resources used for the project (section 3.4) and if applicable with the certificate on financial statement.
- All beneficiaries, in particular non-profit public bodies, secondary and higher education establishments, research organisations and SMEs, have declared to have verified their legal status. Any changes have been reported under section 3.2.3 (Project Management) in accordance with Article II.3.f of the Grant Agreement.

Name of scientific representative of the Coordinator: ....

Date: ..../ ..../ ....

For most of the projects, the signature of this declaration could be done directly via the IT reporting tool through an adapted IT mechanism and in that case, no signed paper form needs to be sent

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[3] If either of these boxes below is ticked, the report should reflect these and any remedial actions taken.

4.1 Final Publishable Summary Report

Executive summary. (1 page)

The basic research target of IOLICAP was the synthesis, optimisation and evaluation of novel Task Specific Ionic Liquids (TSILs) and poly-ionic liquids (Poly-ILs) as solvents that (a) short-term could replace the alkanolamines in the currently applied Post Combustion Capture PCC technology and (b) long-term would lead to the establishment of a novel technology for CO_2 capture, based on hybrid absorption bed / membrane processes incorporating IL modified porous materials and membranes. ILs, due to their high viscosity and cost could never be used as pure solvents for the capture of CO_2. Therefore the main concept of the project was to initially elucidate the effect of water on the CO_2 capture efficiency of ILs and based on this to draw conclusions regarding the most promising type of ILs (chemisorbing or physisorbing) that could totally or partially replace alkanolamines in the chemical process with absorption and still columns. Furthermore, having defined the most appropriate ILs, we had to accurately measure important properties influencing the efficiency (capture and energy) and life cycle of the capture process. These included thermophysical / physicochemical properties, toxicity and corrosiveness of ILs and mixtures of ILs with water and amines. The consortium sought also to unveil the mechanism behind the beneficial influence of ILs in the CO_2 capture process with solvents consisting of mixtures of alkanolamines with ILs. Several mechanisms were examined including the added capture efficiency by sorption in ILs, the synergy with amines via proton abstraction and the high strength of ILs as solvents that can effectively dissolve insoluble carbamates formed between CO_2 and the conventional alkanolamines.

Concerning the application of ILs in the form of Supported Ionic Liquid absorbents and membranes (SILPs and SILMs) we have introduced a highly novel concept. Since the fine dispersion of ILs on high surface area materials was already known to improve the CO_2 capture capacity and rate, our focus was mainly on the optimisation of the materials' morphology towards further enhancements. We therefore brought major new concepts in the morphology and way of SILPs and SILMs development including the "grafting-IL" concept and the "Inverse" SILP concept. In overall we have achieved the synthesis of more than 30 different ILs, 20 SILMs and more than 20 SILPs.

The large number of ILs and supported IL materials developed within the project and our highly ambitious target to fully characterise all the samples, necessitated the commitment of large amount of resources and infrastructures by the Beneficiaries. Specifically four (4) advanced gravimetric sorption analysers were dedicated to the project as well as other advanced equipment for the measurement of key engineering parameters and properties including binary gas/IL diffusivities, self-diffusivities of IL's anion and cation, density, viscosity, surface tension, thermal and electric conductivity, thermal stability, surface morphology, corrosion products, permeability and selectivity. In parallel accurate techniques for the definition of binary gas/IL diffusivities based on dynamic light scattering (DLS) have been developed as well as advanced methods for monitoring the health of the process vessels and elucidating the corrosion mechanism in ILs and mixtures of ILs with amines.

Molecular simulation activities focused initially on the testing and optimisation of existing force fields. The optimized force fields have been validated via molecular simulation test runs using additional experimental data for the most promising ILs. In connection to SILPs and SILMs, the study of confinement effects in the structure and dynamics of the ILs was also performed and finally GCMC calculations were conducted to calculate the adsorption isotherms in carbon nanotubes that were initially selected as supports for the development of SILPs. Thermodynamic modelling activities were mainly related to the optimisation and use of the ePC-SAFT model, accounting explicitly for electrostatic interactions. The results have shown great predictive ability for the solubility of gases in ILs. An important advantage of the proposed model is the transferability of parameters.

Based on the above experimental and theoretical data and implementing a thorough experimental campaign in the lab with several aqueous mixtures of ILs with amines we have defined the best solvent formulation for CO_2 capture consisting of an aqueous mixture of tricyanomethanide (TCM) anion ILs and ethanolamine (MEA). Before upscaling the respective ILs, the effect of ILs purity, corrosion inhibitors and transfer of corrosion products from metallic surfaces to the bulk liquid phase have been examined. It was found that all these parameters had no adverse effects on the CO_2 capture efficiency and rate. As a result, the TCM anion ILs were successfully upscaled at the lowest possible cost. Exploiting the measured thermophysical properties and CO_2 absorption capacity and rate of the TCM ILs and collecting respective data for alkanolamines, we have proceeded with the effective design and construction of the major components (scrubbing and stripping tower and reboiler) and the definition of auxiliary equipment (pumps, blower, heat exchangers) of a Pilot Unit for the treatment of 5000Nm^3/h of flue gas from an NGCC Power Plant, making use of the TCM anion ILs and amines. Preliminary data on the CO_2 capture efficiency and thermal energy requirements allowed us to simulate the Chemical Process and a Thermoelectric Plant *via* appropriate process and thermodynamic cycles software tools and calculate the steam demand and corresponding influence of the capture process on the net efficiency of the Power Plant. Changes in the work plan obliged us to construct and operate the Pilot Unit to capture CO_2 from a thermoelectric plant. Operation for more than half month with MEA solvent and almost one month with the new MEA/IL solvent allowed us to compare the efficiency of the two solvents and draw conclusions on the degradation rate of MEA in the absence and presence of ILs. These results gave valuable input to the LCA analysis of the process.

Regarding the hybrid absorption bed / membrane processes, Inverse SILPs developed with aminoacid anion ILs have shown great CO_2 capture and CO_2/N_2 separation efficiency, while Inverse SILPs prepared with a common IL [BMIM][Cl] were excellent SO_2/CO_2 separation media. Moreover, upscaled SILMs developed on 10 nm pore size mono-channelled ceramic monoliths using the TCM anion ILs were the best performing for SO_2/ CO_2 separation while respective monoliths modified with [EMIM][TfO] exhibited very promising performance for CO_2/N_2 separation. These materials could be implemented in a desulfurization/ CO_2 capture system in series, each one involving a hybrid fixed bed/ membrane process of Class 1-(membrane followed by bed) for same selectivity.

IOLICAP emphasised also on the dissemination of the obtained results towards the scientific community and the general public. The consortium participated in several conferences and published the scientific results in high Impact Factor Journals (6 publications per year (24 total)). Moreover, one CCS Conference was organised in 2013 in Antwerp and one International Forum on CCS was organised in 2015 in Athens attracting +110 and +75 participants respectively. Furthermore, apart from the concrete bilateral collaborations established between the IOLICAP partners, more than 10 master and PhD students as well as 10 post-doctoral fellows have been trained and worked for the project, with a good gender balance.

Summary description of the project context and the main objectives. (4 pages)

The IOLICAP consortium has set the following scientific and technical objectives:

Scientific objectives

1) The development of molecular simulation models for defining the molecular mechanisms that govern the structural, thermodynamic and transport properties of ionic liquids and the application of these models to predict the properties of ILs as well as the dynamical properties of CO_2 and other light gases in ionic liquids. The development of equations of state (EoS) for modelling the ionic liquids (ILs) phase behaviour in CO_2 and other solvents and the performance of GCMC simulations of gas absorption in graphitic materials that can be used as substrates for the ionic liquids to develop SILPs were additional issues addressed in this objective. The consortium had set two major milestones for the achievement of this objective.

The first one (M1.1-month 12) was to develop and validate an EoS model for the phase equilibrium of ILs with gases, achieve the calculation of adsorption isotherms of CO_2, CO and N_2 in SWCNTs and estimate the force field parameters for two IL systems with less than 5% deviation in thermodynamc/structural properties based on available experimental data. In regard to the EoS model, Partner 3 (SC) has integrated the electrolyte PC-SAFT (ePC-SAFT) model in the SciTherm module of their MAPS platform and in this mode, which accounts explicitly for electrostatic interactions, have achieved a great predicting ability for the solubility of gases in [C_4MIM][TCM] and other ILs provided by IT, with the parametrisation of ILs based on density data only. The calculation of adsorption isotherms in SWCNTs was achieved by Partner 1 (NCSRD) via Grand Canonical Monte Carlo (GCMC) simulations considering two models of (9,9) CNTs, an infinite periodic triangular lattice and an isolated bundle. The adsorption isotherms have been calculated as well as the density profiles of the adsorbed gas in the pores and a number of models have been tested for the representation of the gases. The isolated bundle model seemed to predict more accurately the gas adsorption; although some overestimation was observed at low temperatures (~295K) (see Deliverable 1.5). Finally, Partner 1 (NCSRD) implemented also the critical stage of force field validation that took place through the accurate calculation of thermodynamic properties (density). For all systems tested, predicting the densities with less than 1.5% deviation from the experimental values was a prerequisite for the set of parameters to be considered as reliable for the simulation of the ionic liquid. The density values for the three TF_2N anion ILs examined deviated from the experimental ones less than 1.5%.

The second milestone (M1.2-month 18) was to achieve the prediction of light gases permeability in three promising IL systems and calculate the adsorption isotherms of CO_2, CO and N_2 gases in activated graphite surfaces. Regarding the prediction of permeability (Pe) (Pe=DxS where D=diffusivity (cm^2/sec) and S= solubility (mol fraction)), Partner 1 (NCSRD) has used the solubility and diffusivity data for several gases such as CO_2, CH_4, Ar and N_2 in the ILs [C_nMIM$^+$][TF_2N^-], n = 4, 8, 12, [C_nMIM$^+$][TCM^-], n = 2, 4, 8, as calculated by means of molecular simulation using the optimized force field derived in the framework of D1.1 and D1.2. The predictions were in good agreement with the experimental data of Partner 1 (NCSRD) and Partner 6 (TU/e) in what concerns solubility values but there was a deviation of about one order of magnitude from the experimentally derived diffusivities. This discrepancy was solved after the successful development of an advanced Dynamic Light Scattering (DLS) technique by Partner 2 (FAU/SAOT) to experimentally define the binary gas/IL diffusivities in the TCM anion ILs. Comparing with the experimental binary diffusivities of DLS, the predicted permeability properties were in excellent agreement with the experimental ones. For the calculation of the adsorption isotherms of CO_2, CO and N_2 gases in activated graphite surfaces, Grand Canonical Monte Carlo (GCMC) simulations were conducted in a wide range of thermodynamics states (Partner 1). The effect of the activation of the graphitic materials on their absorption capacity was investigated considering two models of (8,8) and (9,9) CNTs: an infinite periodic triangular lattice and an isolated bundle. The isolated bundle model isotherms showed a larger adsorption capacity than the triangular model due to the existence of a gas adsorption layer around the bundle. The activation of the CNTs that takes place mostly near the CNTs' tip and hinders gas penetration inside the activated nanotube, was taken into account by considering part of the nanotubes as "inaccessible" according to nitrogen porosimetry measurements (Partner 1). The density profiles and adsorption isotherms at three temperatures and in a pressure range from 0.1 to 20 bar were in very good agreement with experimental data of Partner 1 (NCSRD).

2) The synthesis and optimisation of aminofunctionalised ionic liquids TSILs, protic ionic liquids PILs and poly-ionic liquids (Poly-IL) and the respective IL/solvent systems (mainly water), which have showed promising CO_2 capture properties above the 0.5 mol/mol limit for CO_2 capture/sequestration. The synthesis of protic ILs (PILs) with enhanced proton conductivity properties and of Poly-ILs that can be applied for reversible SO_2 capture at the 2 mol/mol level. The synthesis of completely novel ILs based on the guidance from WP1. The optimisation of the solvents properties in what concerns their purity, toxicity and absorption properties. The examination of their toxicity and the performance of risk assessment. For the assessment of the successful evolution of work towards this objective we have set four milestones.

The first one (M2.1-month 9) concerned the synthesis of three different amino-functionalised TSILs with CO_2 absorption capacity above 1 mol/mol and 98% regeneration at 80°C and was achieved on time by Partner 2 (FAU/CRT) and Partner 4 (IT) through the development and characterisation of: (a) 1-ethyl-3-methylimidazolium lysinate [C_2MIM][Lys] and its use in mixture with [C_2MIM][TCM] at a molar ratio of 0.23, with the mixture achieving a CO_2 absorption efficiency of 1.85 mol/mol. (b) N,N,N-Trimethyl-N-ethylammonium prolinate [$N_{1,1,1,2}$][Prol] and its inclusion between silica nanoparticles in the form of tiny droplets that achieved CO_2 capture efficiency of 1.58 mol/mol. (c) N,N,N-Trimethyl-N-propylammonium prolinate [$N_{1,1,1,3}$][Prol] and its inclusion between silica nanoparticles in the form of tiny droplets that achieved CO_2 capture efficiency of 1.79 mol/mol.

The second (M2.2 month 12) was the synthesis of three different Poly-ILs that in their solid form would present CO_2 absorption capacity above 2 mol/mol with diffusivity constant exceeding 10^{-6} cm^2/sec. 98% regeneration capacity at 100°C and was achieved by Partner 4 (IT) in collaboration with Partner 2 (FAU/CRT) after defining the proper way of implementation in CO_2 capture, which was the formation of poly-ILs based on IL/chitosan ionogels.

The third (M2.3-month 18) was the synthesis of novel Ionic Liquids with CO_2 absorption capacity close to 1 mol/mol based on physical interaction and regeneration efficiency of 98% at 50°C and was achieved on time by Partner 4 (IT) via the synthesis of ILs with acetate anion, the 1-ethyl-3-methylimidazolium acetate [C_2MIM][OAc] exhibiting absorption capacity of 0.45 mol/mol at 1 bar and 36°C as well as with the synthesis of [C_4MIM][TCM] IL hat exhibited CO_2 absorption capacity of 0.65 mol/mol at 15°C and 15 bar.

The fourth (M2.4-month 24) was the synthesis of highly proton conductive Ionic Liquids with ionic conductivities above 1.5 mS cm^{-1} and was achieved on time by Partner 2 (FAU/CRT) in collaboration with Partner 4 (IT) through the development of [Pyr] formiate and [MePyr] formiate with ionic conductivities of 25 and 15 mS cm^{-1} respectively at 35°C as well as through the synthesis of [C_2MIM][TCM] with proton conductivity of 26 mS cm^{-1} at 35°C.

3) The development of novel techniques for corrosion studies especially focusing to the correlation of the material's performance data with electrochemical measurements and the assessment of the suitability of electrochemical approaches for providing rapid screening of materials. Based on these studies, a further target was to achieve the optimisation of the ILs stability even under extreme conditions involving complex and hostile environments. The two milestones defining the successful evolution of the project's activities towards this objective were:

(M3.1-month 12) The development of a corrosion evaluation methodology strictly adapted to the investigation of ILs. This milestone was met on time by the work of Partner 5 (UoM) and Partner 1(NCSRD) *via* the performance of a wide range of testing including immersion testing of alloys and metals (mild steel, SS 304, SS 316, superpure iron, AA2024-T3 aluminium alloy supplied by Airbus) in the presence of CO_2, O_2, and wide range of temperatures up to 100°C, polarisation behaviour, anodisation tests, tensile strength tests. The suggested techniques for monitoring corrosion and define corrosion products were Scanning Electron Microscopy (SEM) accompanied by energy dispersive X-ray spectroscopy (EDX), Glow discharge optical emission spectroscopy (GDOES), X-ray imaging, combined with SEM/EDX analysis of the alloy, X-Ray Photoelectron Spectroscopy and Plasma Profiling Time-of-Flight Mass Spectrometry.

(M3.2-month 18) The creation of a protocol pertaining to the possible corrosion inhibitor substances (that do not interfere with the IL's absorption capacity) and to the materials of construction in accordance with the chemical composition of the ILs. This milestone was met on time through the collaborative work of Partner 5 (UoM) and Partner 1 (NCSRD). It was showed that some of the ILs themselves (C_8MIM][TCM]) can act as corrosion inhibitors for mild steel in aggressive environments, such as sulphuric and hydrochloric acid and in the presence of CO_2 and O_2 and that sodium molybdate (Na_2MoO_4) had excellent corrosion inhibition capacity without affecting the CO_2 absorption efficiency of ILs and ILs mixtures with amines and water (collaborative work with Partner 6 (TU/e)).

4) The development of advanced techniques for the physicochemical and the thermophysical characterisation of the synthesised ILs with the highest possible accuracy as well as the development of experimental techniques for the rapid screening of the CO_2 and SO_2 absorption capacity under static or dynamic conditions. With the purpose to converge with this objective and due to the large number (more than 30) of different ILs we planned to synthesise and test within IOLICAP the consortium had set three milestones that were met on time.

-The design and construction of two lab-scale prototypes for the rapid screening of the CO_2 absorption capacity of ILs, amines and mixtures of ILs with amines and water (M6).

-The evaluation of CO_2 absorption capacity (solubility) and rate of absorption (kinetics) of at least 20 amino-functionalised TSILs and 10 PILs and of the ionic conductivity of 3 proton conductive ILs (M12) and

-The density, viscosity and surface tension evaluation as function of temperature, amount of CO_2 absorbed and the formulation of the solvent (water-TSIL-corrosion inhibitors) of at least 10 of the most promising TSILs (M24).

One of the prototypes was a milestone for month 6 (M4.1) and was implemented by Partner 1 (NCSRD) through the development of an easily handled high resolution gravimetric system for the measurement of the absorption isotherms of several gases in ILs at several temperatures and up to pressures of 1 bar, giving in parallel the capacity to evaluate the influence of pre-absorbed water on the CO_2 capture efficiency. The second prototype was also a milestone for month 6 (M4.1) implemented by Partner 1 (NCSRD) and consisted of a lab scale experimental set-up simulating the scrubbing/stripping process, where mixtures of ILs with water and ILs with water and amines could be tested for their CO_2 capture capacity in several gas streams containing controllable amounts of CO_2, N_2, and O_2 and where metallic and alloy specimens could be placed and tested for corrosion in contact with the boiling solvent, under repeated cycles of absorption/desorption..

Via a concerted procedure of ILs synthesis and the fruitful collaboration between Partner 2 (FAU/CRT) and Partner 4 (IT) and taking profit from a well-managed exchange of the samples between Partner 2 (FAU/SAOT), Partner 6 (TU/e), Partner 1 (NCSRD) and Partner 4 (IT) we have achieved to evaluate the absorption capacity of 20 amino-functionalised TSILS and 10 protic ILs (PILs) and evaluate the ionic conductivity of more than 5 proton conductive ILs (above the target of 3). A list of the ILs synthesised and examined to achieve this milestone is following presented.

Amino functionalised: (1-ethyl-3-methylimidazolium serinate, 1-ethyl-3-methylimidazolium tryptophanate, 4-ethyl-4-methylmorpholinium serinate, 4-ethyl-4-methylmorpholinium argininate, Guanidinum FAP, 1-ethyl-3-methylimidazolium lysinate, N,N,N-Trimethyl-N-ethylammonium prolinate, N,N-Dimethyl-N,N-diethanolammonium prolinate, N,N-Dimethyl-N,N-diethanolammonium taurinate, N,N,N-Trimethyl-N-propylammonium prolinate, N-ethyl-N-methyl-N,N-diethanolammonium β-alaninate, 1-ethyl-3-methylimidazolium lysinate, and moore than six ionogels with chitosan containing amine groups)

Protic ILs: Severaal ILs were synthesised through the deprotonation of weak proton donors (imidazolide, pyrazolide, triazolide) by a superbase such as (1,8-Diazabicyclo[5.4.0]undec-7-en) (DBU).

Proton conductive ILs: (Pyrollidinium acetate, methylpyrollidinium acetate, pyrollidinium trifluoroacetate, pyrollidinium bis(trifluoromethylsulphonyl)imide, DBUH formiate.

Finally, Partner 2 (FAU/SAOT) in collaboration with Partner 4 (TU/e) achieved not only to provide thermophysical properties of at least 10 ILs as a function of temperature and pressure but also to study the reproducibility and accuracy of the measured properties applying different methods such as oscillating U-tube densimeters, pendant drop and plate methods, dynamic light scattering and surface light scattering methodologies as well as dynamic light scattering of suspended particles.

Technical objectives

1) The optimisation of a continuous flow micro-reactor technology (MCR) for the up-scaled synthesis of the most promising ILs. Since the beginning of the project Partner 4 (IT) provided Partners 1, 2, 5, 6 with adequate quantities (more than 1 kg) of 12 different IL structures to perform the characterisation of thermophysical / physicochemical properties and corrosiveness. The successful implementation of this objective had as milestone for the first period (M6.1-month 18) the synthesis of at least 3Kg of a novel IL, TSIL and PIL exhibiting CO_2/N_2 absorption selectivity of above 1000 at 25-30^{o}C and CO_2 absorption capacity of 1.5-2 mol/mol, (Price 750€/Kg) and was achieved on time. Partner 4 (IT) upscaled the synthesis of [C_2MIM][lys] TSIL in three successive reactions of increasing volume (from 5 to 25L), starting with the reaction between 1-Ethyl-3-methylimidazolium methylcarbonate and H_2SO_4, continuing with the production 1-Ethyl-3-methylimidazolium hydroxide through reaction between [C_2MIM][HSO_4^-] with barium hydroxide octahydrate and ending up with the neutralisation reaction between [C_2MIM][OH^-] with the amino acid (lysine). [C_2MIM][lys] in mixture with [C_4MIM][TCM] gave a CO_2 absorption capacity of 1.85 mol/mol (see 1st periodic report WP2). Protic ILs (PILs) consisting of a super base (DBUH) as cation and imidazolide, pyrazolide and triazolide as anion could be produced at large scale (10 kg/day) via the microreactor technology but despite their high CO_2 absorption capacity (above 1.5 mol/mol) they were judged as unstable during the bubbling with CO_2 and their upscaling was avoided. Instead the continuous flow microreactor technology was optimised (temperature, flow rate, pressure (adjusted via discharge valve), retention time in reactor (length of tube), use of ultrasound source) and the output was the production of 65 kg of each (C_4MIM, C_6MIM, C_8MIM) TCM ILs to be used in the Pilot Unit CO_2 capture Unit at Megalopolis.

2) The development and application of a novel technology based on using Advanced Guided Elastic Waves Methodology for in-situ monitoring the consequences of corrosion into vessels. Partner 10 (NDTech) has achieved the development of a Guided Elastic Waves device (GWD) operating in two modes: (i) the low frequency mode (LFM ~5kHz to 100kHz) where reflections from Guided Elastic Waves at distance as far as 30 meters can be detected by using Micro Fiber Composite (MFC) sensors, and (ii) the high frequency mode (HFM ~100 kHz – 2 MHz), where detection is based on the use of inclined - at appropriate incidence angle – piezoelectric transducers, where range of reflections is limited to a couple of meters. The basic difference between the two modes is that the LFM is capable of obtaining thickness variations due to corrosion at long distances, while the HFM provides high resolution defect detection within the application range. The technology is already applied in the scrubbing tower of the pilot CO_2 capturing unit at Megalopolis.

3) The synthesis and characterisation of Supported and/or Grafted IL Phase Systems based on advanced porous materials (Supported Ionic Liquid Systems SILPS) and membranes (Supported Ionic Liquid Membranes SILMS) and the development and study of Non-Thermal Regeneration Methods involving the synthesised hybrid materials. Four major milestones were set as performance indicators of this objective. Partner 1 (NCSRD) in collaboration with Partner 4 (IT) achieved early in the project the first milestone (M5.1-month 12) which concerned the development of NF ceramic tubular membranes modified with TSILs, exhibiting CO_2/N_2 selectivity of above 300 at 25-30°C and CO_2 permeance of $8x10^{-9}$- $2x10^{-8}$ mol/m^2/sec/Pa, which taking into account the thickness of the membrane's active layer (1.5 micron) corresponds to permeability of 35.8-89.6 Barrer. Membranes developed with the ILs, 1-methyl-3-(3-triethoxysilylpropyl) imidazolium hexafluorophosphate ([spmim][PF_6^-]) *via* grafting (mem 4), [C_4MIM][TCM] *via* physical imbibition on ceramic membranes of different pore size (membranes 5, 11, 12, 18) and [C_8MIM][TCM] *via* physical imbibition on ZIF-69 membrane (mem 20) exhibited CO_2 permeability, CO_2/N_2 selectivity values that brought them above (mem 5), on (mem 20) and just below (mem 4, 11, 12, 18) the upper bound limit of a Robeson plot for CO_2/N_2 separation (see 2nd periodic report section 5.4.6, Fig. 5.4.9). In accordance to the above described performance and taking into account feasibility aspects (mem 5 exhibited high selectivity but moderate permeability and therefore a very high number of membrane tubes would be required to achieve the expected CO_2 recovery) we have selected to upscale ceramic tubular membranes of 10 nm pore size modified *via* physical imbibition with the ILs, [C_4MIM], [C_6MIM] and [C_8MIM] [TCMs]. In this way we have achieved milestone M6.2 (month 24) regarding the development of up scaled (length 50 cm, OD 10 mm) NF membrane tubes with the performance characteristics described in M5.1. Milestone 5.2 (month 15) regarding the synthesis of silica aerogel and its modification with ILs to achieve CO_2/N_2 absorption selectivity of above 500 at 25-30°C and CO_2 absorption capacity of 10mmol/g has been partially achieved (achieved was the synthesis of silica aerogel) and modified (we did not proceeded with its modification with ILs) due to thermal instability (reported in the respective deliverable 5.2). Instead we have utilised mesoporous ordered silica MCM-41 of 2.3 nm pore size and modified it with a silylated IL [spmim][PF_6]. We obtained an astonishing high CO_2/N_2 ideal sorption selectivity value of 1000 and a CO_2 absorption capacity of 1.35 mmol/g. As mentioned in technical objective 1, neutral species in protic ILs (PILs) were extremely volatile when bubbling CO_2 which provided driving force for further deprotonation. We found that it was not worth to proceed with the modification of the membranes utilising PILs, since the membrane process is a continuous flow process where significant leaching can also occur. Instead of this, SILMs with all the series of ILs provided by Partner 5 (IT) have been developed and tested and milestone 5.3 (M5.3-month 18) concerning he preparation of at least three (3) lab scale (length 15 cm, OD 10 mm) NF membrane tubes modified with grafted PILs exhibiting CO_2/N_2 selectivity of above 500 at 25-30°C and CO_2 permeance of $5x10^{-9}$- $1x10^{-8}$ mol/m^2/sec/Pa was achieved by modifying the ceramic membranes with [C_2MIM] [$DePO_4$] and [C_2MIM][TfO].

4) The process engineering and optimisation study of a non-thermal regeneration technology and of the typical scrubbing/stripping technology involving the new solvents. Milestone 7.1 (month 24) was set by the Partners as performance indicator for the achievement of this objective. This was the development of a modeling tool integrating the scrubbing process with the power plant. Partners 8 (N.C.G.), 7 (PPC) and 1 (NCSRD) have implemented the simulated operation of a scrubbing/stripping unit via the Aspen Plus software. There was the demand for using an appropriate thermodynamic model and generalised correlations for the calculation of thermophysical properties and transport properties, as well as to modify databases with parameters that are necessary for the operation of analytical models so that they could reproduce the experimental data. The solvents under study were MEA solvent with concentration of 0.112 mol/mol (mol fraction) (30 wt%) and a mixture of MEA with a chemisorbing IL (MEA/IL = 7:3 mol/mol) with total concentration of the active substances of the order of 0.112 mol/mol (mol fraction). Since the simulation took place based on the mass transport rate (rate based process), for the scrubbing and stripping towers we have used model based on the kinetics of the reactions (REACTION ID MEA-REA ABSORBER/STRIPPER), while for the solution of electrolytes we used the model of Aspen with CHEMISTRY ID MEA where we have made the assumption that the reactions of ions are in chemical equilibrium except from those of CO_2 with OH^- and CO_2 with MEA. The capture of CO_2 by the chemisorbing IL was described by a system of chemical reactions that involve the generation of a zwitterion as is exactly the case with MEA. The simulation results showed that in the first case (reference case) we have specific energy consumption for solvent regeneration of the order of 3.8 GJ/t of captured CO_2 while for the second case (MEA/IL) the respective energy consumption is 3.6 GJ/t CO_2 which is a 6% reduction. The simulations of the thermoelectric unit without and with CO_2 capture (with MEA and MEA/IL) were implemented via the use of thermodynamic cycle modelling software. Partner 7 (PPC) has provided full description of the coal fired thermoelectric plant and the fuel properties to Partners 1 (NCSRD) and 8 (N.C.G.) to perform the simulation of the reference plant including the conditions of the superheated steam, the stages of the super-heater, the conditions of the reheated steam and the stages of re-heating, the positioning of the superheating, reheating and economiser stages from the source to the output of the combustion effluents in the boiler and other important information required to better design the plant. In the simulation of the Ref. Plant with CO_2 capture, the steam is abstracted from the steam turbine at 3.6 bar which is sufficient for the operation of the reboiler ~3 bar, assuming a small pressure drop of 0.5 bar from the point of abstraction to the input of the reboiler. The simulations were performed assuming that a fraction of the flue gas stream of the order of 45% is driven to the CO_2 capture unit and the results showed that the net electric power is reduced by 18.6 MW for capture with MEA and by 17.8MW for capture with MEA/IL compared to the reference plant.

5) The construction of a small-scale pilot unit applying the non-thermal regeneration methods and of a typical Scrubbing/Stripping pilot unit for CO_2 capture from a 5000Nm^3/h flue gas stream where the novel solvents will be tested under real conditions and the performance of Life Cycle Assessment of the process involving the new solvents. The major milestone of this objective (M8.1) was for month 30 (A pilot unit based on the chemical absorption scrubbing process incorporating the new solvent formulations). For reasons we have already explained in the two requests for amendment (No 4 and No 5) regarding the extension of IOLICAP for 15 months, the achievement of this milestone was delayed and accomplished in month 49. The pilot unit was ready in early January 2016 and CO_2 capture tests have been performed until the end of the project (29/02/2016) using: i) MEA solvent 29 Wt % (from 15/01/2016 until 02/02/2016) and ii) Solvent composed of 27.3 Wt % MEA and 5.77 Wt% of a mixture of the ILs [C_2MIM], [C_6MIM] and [C_8MIM][TCMs] (from 5/02/2016 to 23/02/2016). The tests showed a MEA degradation rate of 1.28kg/day when the total amount of MEA in the solvent was 840kg. An important finding was that with the addition of ILs (190 kg in total) the MEA degradation rate drops to 1.26kg per day. This finding, in combination with the improvement of the net efficiency of the thermoelectric plant with CO_2 capture by 0.26% (compared to the CO_2 capture with MEA) constituted the major inputs used for establishing the final exploitation plan and performing an LCA of the process.

Description of the main S & T results/foregrounds. (25 pages)

WP1: Iolicap has achieved the development of molecular simulation models for defining the molecular mechanisms that govern the structural, thermodynamic and transport properties of ionic liquids and the development of equations of state (EoS) for modelling the ionic liquids (ILs) phase behaviour in CO_2 and other solvents. The work was implemented within WP1 with the contribution of Partners NCSRD and Scienomics (SC). WP1 received valuable input from WP's 2 and 4 relevant to the chemical characterisation and purity of the synthesised ILs and the accurate measurement of the ILs and ILs/gas thermophysical properties including, density and viscosity, surface tension, thermal and electric conductivity, self-diffusivities of the cation and anion, gas solubility, binary gas/IL diffusivities and phase equilibrium data of ternary gas/IL/H_2O systems. These data were valuable for testing and validating the accuracy of the developed force fields to predict the dynamic behaviour of ionic liquid systems *via* reliable molecular simulation calculations as well as for the calculation of the binary interaction parameters k_{ij} for mixtures of ionic liquids with gases to be used in tPC-PSAFT EoS models. In line with the objectives of WP5 and 6 regarding the development of absorbents and membranes consisting of IL modified nanoporous materials was also the work implemented by partner NCSRD for the study of gas adsorption of light gases (CO_2, N_2, CO) in graphitic materials in a wide range of thermodynamics states *via* Grand Canonical Monte Carlo (GCMC) simulations and the work performed by partner NCSRD for studying confinement effects in the structure and dynamics of the ILs.

The main S&T results of WP1 were:

1) Validation of the force field showed that calculated densities were in excellent agreement at all cases with experimental data with less than 1.5% deviation from experiment while the transport properties (self-diffusivities and viscosities) which are in general very difficult to capture well, were in very good agreement with the experimental ones. This evaluation procedure rendered the use of the optimized force fields as a reliable basis for the calculation of the macroscopic properties of the ionic liquid families at hand and was also used for the calculation of the transport properties of gases.

The work towards this result was as follows: Partial charges have been calculated for ionic liquids both on isolated ions and on ion pairs using quantum mechanical methodology. Incorporation of polarizability effects was investigated (simulations with Drude polarizable force field [Drude 1900] were conducted) and scaling ions' total charge to lower values was chosen as an alternative simpler way for accounting the charge transfer due to polarizability effects instead of the use a complex and computationally expensive polarizable force field. The optimized force field parameters were validated by performing long molecular dynamics simulations of various schemes and comparing the predicted thermodynamic and transport properties to available experimental data (from WP4) first for selected test ionic liquid systems ([omim][Tf2N], [bmim][TCM). These optimized force fields were further validated for the whole ionic liquid families varying the cations alkyl tail length and in a wide temperature range. Namely, results were extracted for $[C_4mim^+][TF_2N^-]$, $[C_8mim^+][TF_2N^-]$,$[C_{12}mim^+][TF_2N^-]$ and $[C_2mim^+][TCM^-]$, $[C_4mim^+][TCM^-]$,$[C_8mim^+][TCM^-]$ ILs at different temperatures. Force field validation was performed initially through the accurate calculation of densities. Extremely long molecular dynamics simulations have been conducted in order to calculate the transport properties (self-diffusivities, viscosity) of each system and validation of the force fields in use took place though direct comparison with experimental data available by collaborative experimental groups within IOLICAP project.

2) Prediction of permeability of light gases in three promising ILs systems (transport properties) was performed *via* both molecular dynamics and Monte-Carlo simulations using the optimised force field. The results were in excellent agreement with these of the experimental groups.

The work towards this result was as follows: Since the permeability is the product of the gas self-diffusion coefficient and the gas solubility to the ionic liquid, both molecular dynamics and Monte-Carlo simulations had to be performed. For the calculation of the gas self-diffusion coefficient, extremely long molecular dynamics simulations (50-70 ns) were performed at 298 and 363 K and atmospheric pressure, using 10 gas molecules and 100 ionic pairs for each system. The gas self-diffusion coefficient was calculated in the Fickian regime using the Einstein relation. The gas solubility was calculated in the Henry regime using the Widom test particle insertion method. The results for the self-diffusion coefficient were compared to experimental data obtained either from the literature, for the case of the $[TF_2N^-]$ ILs, or from Partners NCSRD, TU/e and FAU for the case of the $[TCM^-]$ ILs. All gas diffusivities were calculated in the infinite dilution limit and are in the order of 10^{-6} cm^2/s, that is, one order of magnitude higher than the ions' self-diffusivities. This is in agreement with the experimental data found in the literature for the case of the $[TF_2N^-]$ ILs. The experimental gas diffusivities in the $[TCM^-]$ ILs were calculated within the framework of IOLICAP by NCSRD, TU/e and FAU, and have been also found to be of the order of 10^{-6} cm^2/s. Gas solubility is proportional to the inverse of the Henry constant that is usually measured by experimentalists. Henry's constant results for CO_2, CH_4, Ar and N_2 were compared to experimental data obtained from the literature for the case of the $[TF_2N^-]$ ILs and with experimental measurements from the IOLICAPs groups within WP4 for the case of the [TCM-] ILs. The Henry's constants of CO_2 and CH_4 in $[C_4mim^+][TF_2N^-]$ were in excellent agreement with the available experimental data.

3) Grand Canonical Monte Carlo (GCMC) simulations were conducted for the study of gas adsorption of light gases (CO_2, N_2, CO) in graphitic materials in a wide range of thermodynamics states. Through this study density profiles and adsorption isotherms were extracted and the obtained results were in agreement to experimental data measured by NCSRD within WP4.

The work towards this result was as follows: Two models of (8,8) and (9,9) CNTs were considered: an infinite periodic triangular lattice and an isolated bundle. The isolated bundle model isotherms showed a larger adsorption capacity than the triangular model due to the existence of a gas adsorption layer around the bundle. The isotherms of both models showed an increase in the adsorption capacity with a decrease in temperature in agreement with the experimental results and correctly predicted a significantly larger amount of adsorbed CO_2 than the other two gases (CO,N_2). The isolated bundle model predicted more accurately the gas adsorption, although some overestimation was observed at low temperatures (~295K), and is able to capture well the pressure dependence of the adsorption process in comparison with the experiment, rendering molecular simulation as very useful predictive tool at thermodynamic states where no experimental data are available.

4) EoS model was extended to include the tPC-PSAFT EoS family and the transferability of the k_{ij} interaction parameter was checked. The ePC-SAFT equation of state was used to model the solubility of CO_2 and other gases in pure ILs and aqueous solutions of ILs and the results were in very good agreement with the CO_2 solubility in TCM anion and Tf_2N anion ILs provided by the experimental groups within WP4. Deviations were observed in the case of ILs with OAc anion at the low pressure region as well as in the case of ternary systems of CO_2/IL/H_2O.

The work towards this result was as follows: The thermodynamic toolkit of the MAPS platform of Scienomics, namely SciTherm, was extended to include the ePC-SAFT model. The above functionalities, made available through a user friendly interface, cover the whole spectrum of calculations from the parameterization of the system to the calculation of volumetric properties, phase equilibrium and gas solubility in systems with ILs. The ILs studied were the imidazolium-based ($C_n$mim, n=2, 4, 6, 8) ILs with the anions BF_4, PF_6, Tf_2N and TCM. The BF_4 and PF_6 were examined for validating the software against available experimental data of the literature. Experimental data for Tf2N and TCM IL families were taken from the literature and from other groups of the IOLICAP project. The ILs were modeled as pseudo-binary mixtures of cations and anions. The ions were parameterized by fitting against density data of different pure ILs containing these ions, simultaneously. This multi-regression approach allowed the transferability of parameters among different ILs. The fitted parameters reproduced very well the density of the ILs as a function of temperature. The solubility of CO_2 and other gases was calculated and found in good agreement with experimental data even without the use of fitted parameters (k_{ij}). This proves that the ePC-SAFT equation of state is appropriate for describing these systems, mainly because it includes electrostatic interactions explicitly, and has therefore a great predictive ability. The effect of water in the solubility of CO_2 was examined for various ILs. In many cases, a discrepancy was found between the experimental trends (from WP4) and the calculations, especially at low sub-atmospheric pressure. Although, various modifications were tried such as different water models, kij parameters, relative permittivity of the medium, the experimental trends could not be reproduced. It seems that the equation of state or the models need to be revisited in order to correct this behavior in the aqueous ILs.

5) Study of the confinement effect on the transport properties of [$Omim^+$][TCM^-] showed a stable, static liquid path in the center of the pore that facilitates the diffusion. The simulations results are consistent with experimental studies in WP5 and 4 on the same confined system.

The work towards this result was as follows: The confinement effects on the structure and the dynamics of 1-methyl-3-octylimidazolium tricyanomethanide [$Omim^+$][TCM^-] IL were studied at various interwall distances using MD simulation. The systems examined consisted of 100 pairs of [C_8mim^+][TCM^-] ions, confined by two solid silica surfaces. The silica surface was described by an integrated LJ potential. The optimized all-atom force field developed and validated within tasks 1.1/1.2 was used for the representation of the IL interactions. All simulations were performed using the LAMMPS software. The initial configurations for the capped, supported and bulk systems were obtained by the amorphous builder as implemented in MAPS software and underwent energy minimization using the conjugate gradient method. Then for the bulk systems a 50 ns run in the NPT ensemble followed using the Nose-Hoover thermostat and barostat in order to obtain the average density, at 398.15 K.

The major foregrounds of this WP were:

- Optimised force field was developed for TCM anion Ionic Liquids and its accuracy validated with long MD simulations against experimental measurements.
- A user friendly thermodynamic model based on e-PCSAFT embedded in to the SciTherm module of the MAPS platform of Scienomics to predict phase equilibrium properties in ILs.

WP2: Within this WP, Partners FAU and IoLiTech have achieved the synthesis of a large number of Ionic Liquids (more than 30 ILs), their chemical characterisation and purity evaluation. Moreover toxicity elucidation of the most promising amongst them was implemented. These ILs included physisorbing ILs, aminofunctionalised ionic liquids TSILs, protic ionic liquids PILs and poly-ionic liquids (Poly-IL) and the respective IL/solvent systems (mainly water). Twelve 12 ILs were produced at the kg scale and sent to the partners from IoLiTech for further characterisation. Three (3) of the most promising ILs were developed at the multi kg scale (65 kg each) and used in the CO_2 capture Pilot Unit within WP8. Based on a review of physicochemical properties of state of the art IL structures IoLiTech provided a list of possible Ionic Liquids that could be synthesised and sent to the Partners in Large Quantities. Decision on the possible structures was made in an informal meeting organised at the University of Erlangen (SAOT School - 29 March 2012). These included a series of ILs based on alkylmethylimidazolium as cation and tricyanomethanide as anion [Rmim][TCM] and a series of ILs based on ethylmethylimidazolium as cation and aminoacids (Lycinate, Serinate) as anion ([emim][Lys] and [emim][Ser]). For the rapid screening of the CO_2 uptake, right after the synthesis, the mass change of IL during CO_2 exposure was monitored by weighting the sample. Furthermore a bubble column for liquids, a gas adsorption apparatus by semi-infinite volume method suitable for ionic liquids and volatile substances and finally a fixed bed apparatus to measure breakthrough curves at solid materials, i.e. invers SILP materials were built up by Partner FAU.
For measuring the self-diffusion coefficient, a number of relevance for all groups engaged in molecular modelling, a NMR method based on DOSY-NMR spectroscopy was established. The eco-toxicity was evaluated via the effect of ILs and mixtures of ILs with water and amines on the photosynthetic efficiency of cyanobacteria (*Chlamydomonas reinhardtii*). Strong efforts were done to synthesise ILs in suitable quality. This implied especially the purification of starting materials and working under clean conditions (i.e. working under inert atmosphere). This activity was of high importance for the application of light scattering methods for the determination of physico-chemical data (developed within WP4 by FAU-SAOT). However the research performed in WP3 and WP4 using conventional techniques showed that neither the presence of impurities nor the presence of corrosion products that are transferred from the metal to the bulk of the IL have any effect on the CO_2 solubility and binary (CO_2/IL) diffusivity. The purity was elucidated with NMR, STIR, ion chromatography and measurement of the water content. Within this WP Partner IoLiTech has also implemented the optimisation of the the microreactor technology for the upscaled synthesis of large quantities of the ILs that have been used in the pilot scrubbing/stripping unit.

The main S&T results of WP2 were:

1) Synthesis of aminofunctionalised ILs and their mixtures with physisorbing ILs (TCM anion ILs) having CO_2 absorption capacity of 1.85 mol CO_2/mol IL.
The work towards this result was as follows: ILs with aminofunctionalised anions were synthesised by a neutralization reaction of commercially available amino acids with EMIM OH and EMMorph OH, respectively. This synthetic route was chosen to avoid the usual way to produce TSILs that involves the displacement of the halide from an organic halide containing the functional group by a parent imidazole, phosphine. Although these synthetic procedures are simple, complete removal of the halide is time consuming, costly, and leads to depressed yields, attributable to inherent loss of the IL during the purification process. Moreover in some applications, halide contamination may not be acceptable, even in ppm quantities. Especially for the application in CO_2 capture, free halides are undesirable since they can have a strong influence on viscosities and corrosion behaviour (together with free amines and free acids). With the neutralisation reaction, four (4) ILs with aminoacid anion were synthesised and characterised by NMR and TGA. The CO_2 absorption capacity was tested in bubbling column and weighing until no mass change. Mixtures of all ILs with [emim][TCM] at a molar ratio of n(TSIL)/n[EMIM][TCM]=0.23 gave the aforementioned high CO_2 sorption capacity for the TSIL with lysinate anion [EMIM][Lys].

2) Synthesis of aminofunctionalised ILs and their embedment between silica nanoparticles sleeves in the form of tiny droplets, creating a flowing liquid powder termed as Inverse SILP. The Inverse SILP with N,N,N-Trimethyl-N-propylammonium prolinate IL had achieved maximum capture efficiency of 1.79 mol/mol at 40°C and 15 vol.% CO_2.
The work towards this result was as follows: ILs with aminoacid anions (taurinate and prolinate) and alkylammonium cations were synthesised by three successive steps. First reactions of tertiary amines with bromoalkanes followed by conversion of the produced bromide IL to hydroxide IL via a strong basic ion exchange resign. The final step was neutralisation reaction with an aminoacid. The produced ILs were enclosed at contents of 40-50% weight between silica nanoparticles via a simple and easily upscalable phase inversion process where a slurry of the IL and silica in solvent (ethanol) was heated allowing for the solvent to evaporate. The procedure for testing the CO_2 capture efficiency was via breakthrough curves in in fixed beds in a stream containing 15 vol.% CO_2.

3) Synthesis of Poly-Ionic Liquids based on the formation of chitosan /IL ionogels and their enclosure between silica nanoparticles forming Inverse SILPs embedding ionogel phase. These ILs performed at a CO_2 capture efficiency of 0.5 mol

fraction (-) at 15 vol. % CO_2, but their SO_2 capture efficiency was astonishing reaching values of 0.5 mol fraction (-) in a stream containing only 0.13% SO_2.

The work towards this result was as follows: The work here passed through the synthesis of a variety of poly-ionic liquids until a conclusion had been drawn that the best candidates for a CO_2 capture application were the biopolymer based ionogels enclosed between nanoparticles of pyrogenic silica. The synthesis of poly-ILs was a multistep process, in which first the monomeric IL was constructed, isolated and purified, and then subjected to polymerisation. A further variable we have tried in this process was whether the ion exchange occurs at the monomer stage or after polymerisation. We tried both approaches for the synthesis of several poly-ILs (Poly [1-(para-vinylbenzyl) pyridinium tetrafluoroborate] (P[VBP]-[BF4]) and Poly [1-(para-vinylbenzyl) triethylphosphonium tetrafluoroborate] (P[VBTEP][BF4]) by doing the anion exchange before the polymerisation, i.e. with the monomer, or after polymerisation with the poly(IL). Moreover, the respective poly-ILs with bis(trifluoromethylsulfonyl)imide (BTA) anion and chloride anions were synthesised and tested as well as poly-ILs such as Poly(benzylvinylpyridinium) bis(trifluromethylsulfonyl)imide and Poly(benzyl-methyl-aminopropylacrylate also as a bis(trifluromethylsulfonyl)imide salt. In all these cases the products were either a solid, or a sticky black mass, which could not be properly analysed, purified or handled. Because of these problems, combined with the very high viscosity of the materials, which reduced considerably the sorption of CO_2 into them (results on their CO_2 soprtion capacity are included in the second periodic report WP6), we found that poly-ILs are not suitable for direct CO_2 capture, but might be used as membrane materials. As alternative, the use of aminogroup-containing biopolymer chitosan as a solution in ionic liquids (forming so called ionogels) was proposed by our partner FAU and the results showed that we had indeed a very good sorption capacity especially for SO_2.

4) Synthesis of three types of protic ILs (PILs) based on the reaction deprotonation of Imidazolide, Pyrazolide and Triazolide by a super base. These ILs, although seemed very promising for CO_2 capture having the capacity to absorb high CO_2 amounts, they have been proved unstable. This is due to the fact that the protonation reaction is reversible and the charged species are in equilibrium with their neutral starting materials. Although PILs were supposed to behave like aprotic ILs with considerably reduced vapour pressures, under certain reaction conditions the deprotonation of the cation was favoured. We have there volatility of the neutral species which provides driving force for further deprotonation.

The work towards this result was as follows: As super base we have used DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) belongs to the class of amidine compounds and has a pH value of 12.8 (10 g/l, H_2O, 20 °C). The novel PILs were synthesized in high yield (> 98%) by protonation of DBU with imidazole, pyrazole, or triazole. The structures of these PILs were confirmed by NMR spectroscopy the water content and viscosity was also measured. For example, bubbling of the CO2 through the PILs containing solution provides the absorption reaction on the one side, but also “leaching” of the neutral starting material on the other side.Bubbling of the CO_2 through the PILs containing solution provided the absorption reaction on the one side, but also “leaching” of the neutral starting material on the other side.

5) Physisorbing IL with tricyanomethanide anion [Omim$^+$][TCM$^-$] provided by Partner (IoLiTech) exhibited high SO_2 absorption capacity of the order of 0.5 mol/mol at 850mbar and 36°C. Guanidinium lactate based ionic liquid [TMGB2] [BTA] was also synthesised by neutralisation reaction with the acid HBTA in ethanolic solution. The absorption capacity was of the order of 1.2 mol/mol at 850 mbar and 36°C. What is more, we have also synthesised and tested ILs with alkylammonium cations and prolinate, taurinate alanate anions as well as ionogels of chitosan with 1-butyl-3-methyl imidazolium methoxyethoxyethyl methyl phosphonate [EMIM][Me(EG)$_{2(}$Me)PO$_3$] and [BMIM][Cl]. The later showed the most promising SO_2 absorption capacity of 0.5 mol/mol which was highly reversible with regeneration at only 60°C under vacuum. The aminoacid anion ILs (N,N-dimethyl-N,N-diethanolammonium prolinate [N$_{1,1,2}$-OH$_{,2}$-OH][Prol] N,N,N-trimethyl-N-ethylammonium prolinate [N$_{1,1,1,2}$][Prol], N,N dimethyl-N,N-diethanolammonium taurinate [N$_{1,1,2}$-OH$_{,2}$-OH][Tau] and N-methyl-N-ethyl-N,N-diethanolamonium β-alanate [N$_{1,2,2}$-OH$_{,2}$-OH][Ala]) although exhibited higher SO_2 absorption capacity (0.8 mol/mol) they suffered of poor regeneration ability.

The work towards this result was as follows: [OMIM][TCM] was synthesised purified and chemically characterised (NMR) by Partner IoLiTech who also provided data on its purity (ion chromatography) and thermal stability. The procedure followed was the one implemented for all ILs with tricyanomethanide anion that were judged as the best candidates to replace fraction of MEA in the Pilot Unit for CO_2 capture. Partner FAU synthesised [TMGB$_2$] [BTA] by neutralisation reaction and [EMIM][Me(EG)$_2$(Me)PO$_3$] and [BMIM][Cl] ionogels by dissolving certain amount of chitosan in to the respective ILs. Then a phase inversion technique was applied to enclode droplets of the ionogels into porous sleeves of silica nanoparticles. All of the SO_2 absorption tests were performed within WP4 at NCSRD’s and PPC’s facilities.

6) A microreactor technology (MRT) existing at IoLiTech labs has been adapted for reactions in the Liquid Phase, such as alkylation reactions for the upscaled production of the three ILs with TCM anion, selected for use in the large CO_2 capture Pilot Unit. The two main factors in the MRT technology (reaction temperature and flow rates)- are influenced by two main structural motifs: the chain length of the alkylating agent and the type of the chosen anion (chloride or bromide). Therefore the MRT technology was also optimised towards the upscaled synthesis of TCM anion ILs with butyl,- hexyl- and octyl chains on their

imidazolium cation. The final achievement was the production of 65 kg of each one of the ILs [BMIM][TCM], [HMIM][TCM] and [OMIM][TCM].
The work towards this result was as follows: The most important factors that needed to be considered were the temperature and flow rate. These are depending on the chain length of the chosen alkylating agent and its leaving group, since an alkylbromide is more reactive than its chloride analogue. For the production of two alkylimidazolium halides, i.e. 1-hexyl-3-methylimidazolium bromide (HMIM Br) and 1-octyl-3-methylimidazolium bromide (OMIM Br) different parameters were examined in order to find the optimal conditions. The reactions were carried out at 80 - 120°C, the retention time was varied by the length of the tube. In both reactions the pressure was adjusted to 80 psi (5.52 bar) by use of a discharge valve and in both reactions 1.05 equivalents of the alkylating agent were used. The results obtained from the alkylation with hexylbromide and octylbromide showed that the best performances were achieved for HMIM Br at 100°C with flow rates of 4 and 7.36 ml/min, respectively. For OMIM Br flow rates of 8 and 18.4 ml/min, respectively, and heating to 120 °C led to the best performance.

The major foregrounds of this WP were:

- Mixtures of TCM anion based ILs with water, having enhanced CO_2 capture capacity and faster capture kinetics than the bulk IL.
- Microreactor technology for the upscaled synthesis of TCM anion based ILs having the great advantage of shortened reaction time due to better surface to volume ratio and less side reactions because of the avoidance of hot spots during the reaction. Moreover the technology reduces the solvent wastage since the starting materials react without the need of any solvent.
- Inverse SILP absorbents as a new concept for Supported Ionic Liquid Phase materials having exceptional capacity for both CO_2/N_2 separation and SO_2/CO_2 separation depending on the IL phase enclosed into the SILP.

WP3: Within this WP, Partners UM and NCSRD after having reviewed the relevant mechanisms of corrosion and corrosion prevention in conventional aqueous systems and the latest studies of corrosion of a number of metals and alloys in ionic liquids, have further proceeded with the performance of thorough investigations that were focussed on the corrosion behaviour of alloys of primary interest for CO_2 capture in the presence of ionic liquid solvents. The work addressed the corrosion performance of stainless steel of types 304 and 316, mild steel (MS), the aerospace AA2024-T3 alloy and pure Iron as reference, in the twelve (12) types of received ionic liquids (ILs) prepared by partner IOLITEC (IT) as well as in amine solvents such as MEA, DEA and MDEA and in solvents consisting of aqueous mixtures of the aforementioned amines with ILs. Especially AA2024-T3 aluminium alloy was selected because possible interaction of intermetallics with aluminium matrix in ILs might help better understand interaction of inclusions with iron in MS in ILs. AA2024-T3 is widely used in the aerospace industry for its damage tolerance, relatively high tensile strength and high strength to weight ratio. These properties are achieved by appropriate alloying with copper and magnesium which, in addition to strengthening phases, form copper- and magnesium-containing constituent particles. As a consequence, the presence of alloying elements renders the alloy susceptible to localised corrosion, with many studies dedicated to protection of the alloy.
The tests were performed by immersing specimens of the metals in plastic bottles containing the IL, for several days and at various temperatures (up to 100°C) in the presence or not of water, as well as by performing immersion tests in the reboiler section of a lab scale scrubbing/striping device developed by Partner NCSRD for the purposes of the project. In this way it was possible to simulate the real conditions and test the corrosiveness in the presence of O_2 into the feed stream, under continuous flow of the solvent and at temperatures above 100°C. In parallel Partner NDTech worked on the development of a working prototype of a guided wave device (GWD) for monitoring the health (thickness and formation of pinholes) on large cylindrical vessels. Amongst the several ILs tested including the1-methyl-3-ethylimidazolium tricyanomethanide, [C2mim]TCM, 1-methyl-3-butylimidazolium tricyanomethanide, [C4mim]TCM, 1-methyl-3-hexylimidazolium tricyanomethanide, [C6mim]TCM (pure and standard batch). 1-methyl-3-octylimidazolium tricyanomethanide, [C8mim]TCM, 1-methyl-3-ethylimidazolium lysinate, [C2mim]L, 1-methyl-3-ethylimidazolium serinate, [C2mim]S, Pyrrolidium-2-one trifluoroacetate, [BHC]TFA, Pyrrolidium-2-one bis(trifluoromethylsulfonyl)imide, [BHC]BTA, 1-methyl-3-ethylimidazolium acetate, [C2mim]OAc, 1-methyl-3-ethylimidazolium diethyl phosphate, [C2mim]DP, [1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium] tricyanomethanide, [1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium]TCM, it became obvious from the very beginning of the project that those with the tricyanomethanide anion had very good behaviour regarding corrosiveness and in some cases (those with longer alkyl chains in their imidazolium cation) could even act as corrosion inhibitors. Therefore a major focus was on these ILs and their behaviour in mixtures with water and amines as well is their CO_2 capture efficiency in the presence of corrosion inhibitors and impurities dissolved in the IL from the metallic surface. On this purpose there was a very strong collaboration between the Partners involved in WP's 3 and 4.
The tests performed in overall were immersion testing, tensile testing, anodization and polarisation while a multitude of advanced analytical techniques were devoted to the characterisation (chemical and morphological) of the specimen's surface

after the tests to extract conclusions on the corrosion products and mechanisms. These included scanning electron microscope equipped with BSE and EDX detectors, Glow Discharge Optical Emission Spectrometry, X-Ray Photoelectron Spectroscopy, X-Ray Imaging and micro-Raman spectroscopy.

The main S&T results of WP3 were:

1) Both 304 and 316 stainless steel are not affected after immersion in [C_4mim]TCM for 3 days. No changes were revealed in the surface morphology from SEM examination and in the chemistry of the near-surface region from GDOES elemental depth profiling. Immersion of type 304 stainless steel in [BHC]BTA resulted in dissolution of sulphide inclusions, leaving the macroscopic surface nearly unaffected.
2) Generally, the surface morphology of MS changes in all TCM anion ILs at a temperature of 80°C during immersion from 1 h to 10 days. The changes are initiated in the areas adjacent to MnS inclusions and are accompanied by generation of craters, comprising cavities in the middle, surrounded by corrosion products defined as those with increased oxygen contents according to EDX analysis. The phase compositions of the corrosion products were identified by micro-Raman mapping at NCSRD to be mixed magnetite/maghemite oxides forming preferentially at the areas surrounding the inclusion sites. Corrosion products were generated in [C_2mim]TCM and [C_4mim]TCM, whereas no significant changes to the surface morphology were observed after immersion in [C_6mim]TCM and [C_8mim]TCM at 70 ºC.
3) Addition of up to 3 % water in [C_8mim]TCM does not result in significant increase in generation of corrosion products on the surface of MS during immersion at 80 °C. Thus, the previously observed increase of the coverage of the surface of MS with corrosion products after immersion in the IL in the order [C_8mim]TCM ~ [C_6mim]TCM < [C_4mim]TCM < [C_2mim]TCM may be associated with the length of alkyl chain in the cation, e.g. the number of carbon atoms in the chain, rather than with water contents in the IL. Further increase of water content to 5 % in [C_2mim]TCM and [C_8mim]TCM results in slight dissolution of metal over the macrosopic surface during immersion testing and increases the dissolution rate of MnS inclusions. Immersion of MS in [C2mim]TCM with 5 % water at 70°C results in dissolution of the majority of the MnS inclusions within 2 h of immersion.
4) Corrosion products were not detected after immersion testing of pure iron in [C_2mim]TCM that was attributed to the absence of MnS inclusions in the metal matrix
5) Immersion of MS in the amine-functionalised ionic liquids [C_2mim]L and [C_2mim]S results in the dissolution of metal over the macroscopic mild steel surface. In contrast to TCM- anion-based ILs, MnS inclusions are not totally dissolved within 3 days of immersion. The odour released from these ILs may be related to the chemical instability of the ILs. The aggressive behaviour of these amino acid-based ILs and their corrosivity may significantly impair their application potential as solvents for post-combustion CO_2 capture, despite their high CO_2 absorption capacity.
6) The results on the corrosion behaviour together with the marked enhancement of the CO_2 absorption capacity of binary TCM anion-based ILs/H_2O mixtures established in WP4, renders this type of ionic liquids to be very promising for CO_2 separation applications. In particular, TCM anion-based ionic liquids with the longer alkyl chain length offer enhanced CO_2 solubility, high thermal stability and low viscosity, while mitigating efficiently corrosion in low cost metallic substrates such as mild steel.
7) [BHC]TFA and [BHC]BTA severely attacked the surface of mild steel, leading to dissolution of metal over the entire surface and significant weight loss at both room temperature and 80 °C. The dissolution rate significantly increased with increase of temperature. Molybdate efficiently inhibits etching over the macroscopic surface of MS in [BHC]BTA at concentration of 500 ppm at both room temperature and 60°C. In contrast, addition of 10^{-2} M thiourea to [BHC]BTA did not reduce the corrosivity of the IL. Thus, the required inhibitor should be selected individually for each IL, with a detailed study of its effect on the IL functionality.
8) Immersion of MS in [C_2mim]OAc and [C_2mim]DP resulted in dissolution of MnS inclusions without generation of significant amounts of corrosion products. This may be attributed to corrosion inhibition effect of the ILs through the adsorption on the metal surface and blocking active sites surrounding MnS inclusions.
9) A mechanism underlying MnS-induced corrosion of MS in ILs with TCM anion is proposed. Corrosion initiates at the sites of MnS inclusions on the surface of MS, resulting in the formation of cavities due to the MnS dissolution, which may be surrounded by corrosion products containing magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). The amount of the corrosion products generated around the inclusion sites decreased with the increase of the cation alkyl chain length, following the order [C_2mim]TCM > [C_4mim]TCM > [C_6mim]TCM~[C_8mim]TCM. This was attributed to the corrosion inhibition effect of the ILs through adsorption on the metal surface and blocking active sites, with the inhibition efficiency increasing with the alkyl chain length. The underlying mechanism was associated with corrosion processes at active sites on the MS surface, such as sulphide inclusions, in the presence of residual water and oxygen in the IL. It was shown that increase of the water content in the ILs to about 50000 ppm resulted in faster dissolution of the MnS inclusions. Finally, it was demonstrated that removal of oxygen from the IL significantly reduced the corrosion rate.
10) Immersion of MS in [1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium]TCM results in formation of craters at MnS inclusion sites accompanied by dissolution of inclusions; no corrosion products were detected by SEM/EDX examination.

11) Testing of MS was implemented in the reactor at NCSRD and in the laboratory conditions at The University of Manchester, employing the aqueous mixtures of DEA/MDEA and DEA/MDEA/[C_4mim]TCM/[C_6mim]TCM/[C_8mim]TCM. The behaviour of MS in the mixtures of amines and amines/ILs is similar at immersion durations from 3 to 10 days. The immersion results in etching of the alloy surface at the pearlite regions, leaving ferrite regions intact. Further, during immersion, MnS inclusions dissolve without generation of corrosion products in the areas surrounding the inclusion sites. In contrast, testing in the reactor at NCSRD resulted in severe attack of the alloy in the mixture of DEA/MDEA due to the presence of significant amounts of dissolved oxygen and carbon dioxide in the solvents. Further, the fast flow of the solvents in the reacted contributed to the generation of corrosion products. On the other hand the surface of MS in the DEA/MDEA/[C_4mim]TCM/[C_6mim]TCM/[C_8mim]TCM appeared featureless in the Raman analysis showing that the solvent proposed for use in the upscaled Pilot Unit is less corrosive something that was highly important for the commercialisation potential of the new solvent.

The major foregrounds of this WP were:

- Novel experimental protocol for the rapid screening of the corrosive strength of Ionic Liquids.
- CO_2 capture capacity and rate of TCM anion ILs is not affected by the corrosion products and corrosion inhibitors.
- A device implementing the GWD principle of measurement for monitoring the health (metal thickness, formation of pinholes and craters) of large metallic vessels.
- TCM anion based ILs with long alkyl chains as corrosion inhibitors for mild steel.

WP4: Within this WP, Partners TU/e, FAU and NCSRD implemented the thermophysical and physicochemical characterisation of all the ILs provided by IoLiTech (12 different IL structures) while most of the equipment used for the elucidation of the gas absorption capacity in ILs (IGA gravimetric systems and Magnetic Suspension microbalances) was also appropriate for measuring the gas absorption capacity of the SILP and Inverse SILP materials. The properties of interest were the density, viscosity, surface tension, thermal conductivity, thermal stability, electric conductivity, gas solubility and binary gas/IL diffusivity of pure ILs as well as the excess properties (viscosity and density) of mixtures of ILs with water and were measured with the highest possible accuracy by Partners FAU and TU/e. NCSRD had as major task the rapid screening of the gas absorption performance of ILs. For that reason an existing full-beam, force restoration microbalance was connected to a special gas manifold including the possibility to add water vapor in order to examine the effect of pre-absorbed water on the CO_2 capture efficiency of ILs. Moreover a small scale scrubbing stripping device was constructed and operated that provided the opportunity to test aqueous solutions of ILs and aqueous mixtures of ILs with amines in a process that simulated the process implemented in the Pilot Unit (deliverable WP8). This device and the performed experimental campaign assisted in the definition of the most appropriate solvent to be used in the Pilot Unit; e.g. a mixture of TCM anion based ILs with MEA. Since the low viscous tricyanomethanide ([TCM]$^-$)-based ionic liquids (ILs) had showed, early in the project, very promising corrosiveness and thermal stability characteristics and the rapid screening procedure gave satisfactory results regarding their CO_2 capture efficiency, they have gained increasing interest as attractive fluids for application in the Iolicap project. Therefore, the characterization of [TCM]$^-$-based ionic liquids comprised an extended compilation of novel data in what concerns several thermophysical properties and CO_2 solubilities. The work combined experimental, simulation and equation of state modeling studies and provided relevant information and trends for this less-characterized class of ILs. The publications produced in this consortium will have a significant impact on the field because CN-based ILs have attracted more and more the attention of IL communities due to their interesting properties, for instance substantially lower viscosity compared to the "conventional" ILs with [Tf_2N]$^-$ and [BF_4]$^-$ anions. A thorough comparison with existing experimental data and those of other ILs families has been performed to investigate structure-property relationships.

The chemical modifications of the cation's alkyl chains by incorporating ether- and hydroxyl groups affects the thermophysical properties and CO_2 solubilities. Besides, ether groups incorporated into the alkyl chain improve the biodegradability of imidazolium-based ILs and compounds containing hydroxyl groups provide sites for enzymatic hydrolysis resulting in increased aerobic biodegradation.

The miscibility of the [TCM]$^-$-based ILs with water, due to the hydrophilic nature of this family of ILs (the formation of hydrogen bonds between the water molecules and the anion), decreases their viscosity and leads to a positive excess volume. Our partners from Demokritos have investigated the impact of these changes in properties on the CO_2 absorption and concluded that the CO_2 absorption capacity is enhanced by diluting the ILs with water. More specific, NCSRD and TU/e, having developed a method of testing the effect of water on the CO_2 absorption of the TCM anion ILs, concluded to an astonishingly high positive effect of pre-absorbed water on the CO_2 capture efficiency of the TCM anion based ILs while the effect on acetate anion ILs was negative and the effect of Tf2N anion ILs was inappreciable. The positive effect was explained via a combination of excess property measurement and advanced spectroscopic techniques (micro Raman) that shed light to a mechanism of more free volume generation in the IL due to dissolution of small portions of water. Having concluded to the potentiality of TCM anion ILs the thermophysical properties (density, viscosity, surface tension, electrical conductivity) of the 1-alkyl-3-methylimidazolium tricyanomethanide [$C_n$mim][TCM] (n = 2, 4, 6, 7, 8) IL series were experimentally measured over the temperature range from 288 to 363 K. Moreover, a classical force field optimized by our partners (NCSRD) within the IoLICap project for the imidazolium-based [TCM]$^-$ ILs was used to calculate their thermodynamic, structural and transport properties (density, surface tension, self-diffusion coefficients, viscosity) in the temperature range from 300 to 366 K. The predictions were directly compared against the experimental measurements. The effects of anion and alkyl chain length on the structure and thermophysical properties have been evaluated. In cyano-based ILs, the density decreases with increasing molar mass, in contrast to the behavior of the fluorinated anions, being in agreement with the literature. The contribution per $-CH_2-$ group to the increase of the viscosity presents the following sequence: [PF_6]$^-$ > [BF_4]$^-$ > [Tf_2N]$^-$ > [DCA]$^-$ > [TCB]$^-$ > [TCM]$^-$. [TCM]$^-$-based ILs show lower viscosity than dicyanamide ([DCA]$^-$)- and tetracyanoborate ([TCB]$^-$)-based ILs, while the latter two exhibit a crossover which depends both on temperature and the alkyl chain length of the cation. The surface tension of the investigated ILs decreases with increasing alkyl chain length. [C_2mim][TCM] shows an outlier behavior compared to other members of the homologous series. The surface enthalpies and surface entropies for all the studied systems have been calculated based on the experimental surface tensions. The relationship between molar conductivity and viscosity was analyzed using the Walden rule. The CO_2 solubilities and absorption kinetics have been reported previously.

Furthermore, the thermophysical properties (decomposition temperature, glass transition temperature, density) and viscosity of imidazolium-based ionic liquids (ILs) paired with the tricyanomethanide ([TCM]$^-$) anion and the bis(trifluoromethylsulfonyl)imide ([Tf_2N]$^-$) anion were studied within a wide temperature range. The effect of the ether-functional group (in [Tf_2N]$^-$ and [TCM]$^-$ ILs) and hydroxyl-functional group (in [Tf_2N]$^-$ IL) incorporated in the cation's alkyl chain on the thermophysical behavior and carbon dioxide (CO_2) solubility was evaluated by comparing their behavior to the corresponding non-functionalized ILs. The thermal stability was enhanced by the inclusion of hydroxyl-functionalization in the cation's alkyl chain while ether-functionalization had no major effect on the thermal stability. The ether groups (one or two) resulted in an increase in the density and a decrease in the viscosity of all ILs. The hydroxyl group resulted in an increase in both properties. The CO_2 solubilities were not affected by the presence of the ether groups, while the hydroxyl group led to a significant decrease in the solubility. Additionally, the ePC-SAFT equation of state was used by our partners (Scienomics) to calculate the CO_2 solubility in the ILs and the Henry's law constant. The model showed great predictive ability. The Henry's constants were applied to calculate the partial molar thermodynamic properties of solvation.

FAU had also a significant contribution in the accurate determination of the binary (CO_2/IL) diffusivities. After altering a limitation in the application of their advanced DLS (Dynamic Light Scattering) technique in coloured samples (*via* purification of the ILs) they had achieved to provide highly accurate results and what is more, resolve a problem of discrepancy between the experimentally and molecular simulation derived permeability in ILs. This discrepancy existed between the results provided by the experimental groups of NCSRD and TU/e and the theoretical group of NCSRD and was attributed to the fact that the gravimetric technique included the macroscopic mass transport in the calculation of the binary gas/IL diffusivities.

The main S&T results of WP4 were:

1) The addition of small quantities of water (up to molar fraction of 0.7) into the ILs [$C_n$mim][TCM]with n=4 and 8 provoked a 4-5 times higher CO_2 capture efficiency and 3-4 times higher absorption rate. This result was elucidated with a new methodology derived by Partners NCSRD and TU/e and was an additional motivation for the use of this type of ILs in mixtures with amines in the Pilot Unit.

2) The structure-property relationship of the cyano-based ILs is extensively discussed using both experimental data and molecular simulation results. As expected, the densities of the [TCM]$^-$-based ILs decrease with increasing temperature. Additionally, a decrease of the densities with increasing alkyl chain of the imidazolium cation is observed.

3) The effect of the anion on the densities of 1-alkyl-3-methylimidazolium based ILs has been evaluated. For ILs with cyano anions the density decreases with increasing molar mass. This is related to differences in the structure observed in RDFs calculated from molecular simulations. [C_4mim][TCM] exhibits a weaker ion pairing that is also supported by quantum mechanical calculations that resulted in a smaller total ionic charge compared to the ones extracted in a similar manner for the [C_4mim][Tf_2N] system. The fluorine-based ILs show higher densities than the ones containing cyano-anions, a fact that could be partially attributed to the contribution of the heterogeneous and heavy atoms. In addition, the shape/symmetry and strong ionic interactions of fluorine-based ILs enhances a more selective distribution around the charged cation. This can be related to a higher structural organization in the bulk liquid, leading to higher densities. Moreover, compared to the cyano-based ILs, a reverse trend is observed for ILs with fluorinated anions, that is the density increases with increasing molar mass.

4) Both [DCA]$^-$- and [TCB]$^-$-based ILs show a higher increase in the viscosity with increasing alkyl chain length compared to the [TCM]$^-$-based ILs. Furthermore, [DCA]$^-$- and [TCB]$^-$-based ILs show a switch in the viscosity, which is influenced both by the alkyl chain length and the temperature. The lower viscosity of the studied [TCM]$^-$ ILs could be connected with the more uniform

distribution of the anion around the cation contributing to a higher fluidity as a result of the weaker anion-cation interaction. A higher viscosity is observed for fluorinated-based ILs, which decreases as the size of the fluorinated anions increases.

5) The surface tension decreases with increasing the alkyl chain of the [$C_n$mim][TCM] IL series, with the exception of [C_2mim][TCM] that exhibits slightly lower values than the ones of [C_4mim][TCM] ILs. The effect of the anion in this property was more complex to evaluate due to the large number of different techniques and not stated impurities (e.g. water) which affect the experimental data. Nevertheless, the cyano- and [PF_6]$^-$-based ILs show higher surface tensions within the same range. Lower surface tensions, surface enthalpies and entropies are observed for [$C_n$mim][Tf_2N] ILs. In general, the surface enthalpies decrease with increasing alkyl chain of the cation, while the surface entropy does not show a clear dependency on the alkyl chain length. As expected the electrical conductivities decreases with increasing alkyl chain length. The data are described using VFT equation. The [TCM]$^-$-based ILs belong to the group of glass forming systems. The molar conductivities are calculated considering the densities and electrical conductivities. [TCM]$^-$ ILs show similar iconicity as [$P_{6,6,6,14}$][Cl], being classified as intermediates between true ILs and true molecular liquids.

6) The chemical modification of the alkyl chain of imidazolium-based ILs by incorporation of ether and hydroxyl functional groups has influence on the thermophysical properties and CO_2 solubilities. Both families of ILs investigated in this work, those containing the [TCM]$^-$ anion and the [Tf_2N]$^-$ anion, are thermally stable and show a wide liquidus range. Ether-functionalized cations with short chains were found to have no major effect on the thermal stability compared to their alkyl-substituted analogues. On the other hand, the introduction of a hydroxyl group at the end of the chain increases the decomposition temperature, resulting in a thermally more stable IL. This could be attributed to the additional hydrogen bonds between the ions that involves more energy to break. By relating the relative weight of the ions to that of the entire IL it was possible to state that in the [TCM]$^-$-based ILs the anion decomposes first, followed by the cation and that the anion plays an essential role in the decomposition process. The [Tf_2N]$^-$ ILs decompose without a clear difference between the anion and the cation. To determine the long term stability, all ILs were subjected to 423 K for 12 h, the minimum weight losses could be attributed to the presence of moisture and volatiles.

7) [Tf_2N]$^-$ ILs show a higher mass density than [TCM]$^-$ ILs. The hydroxyl group has a larger impact on the density increase than the ether group. The higher densities of the oxygenated ILs could be explained by the hydrogen bonds between the ions resulting in a denser packing.[Tf_2N]$^-$ ILs show a higher dynamic viscosity than [TCM]$^-$ ILs. The ether-functionalized ILs have lower viscosity compared to their alkyl-substituted counterparts. This could be related to the higher flexibility of the chain, which causes a higher molecular motion. The hydroxyl-grafted IL shows a higher viscosity due to the additional attractive contribution by hydrogen bonding leading to an increase in the cation-anion interactions.

8) The effect of the ether groups on the CO_2 solubility is negligibly small. Furthermore, the CO_2 solubility is more dependent on the anion (higher solubility in [Tf_2N]$^-$-based ILs than [TCM]$^-$-based ILs) than the cation. On mass fraction base the CO_2 solubility is slightly higher in the [TCM]$^-$, because of their smaller molecular weight. The CO_2 solubility decreases by the introduction of the hydroxyl group in the imidazolium-IL of [Tf_2N]$^-$ anion due to a less favorable entropic contribution. The Henry's law constants and the partial enthalpy and entropy of absorption reflect the physical nature and indicate the exothermal behavior of the CO_2 absorption process by the ILs investigated.

9) The solubility of CO_2 in the ILs was also modeled with ePC-SAFT, which is one of the most suitable EoS models for these systems, since it accounts for electrostatic interactions. The solubility of CO_2 calculated at various temperatures and pressures up to 2 MPa was found to be in good agreement with the experimental data even without the use of adjustable parameters. This work is a complete contribution to the better understanding of the interesting properties of [$C_n$mim][TCM] ILs and those with functional groups in the cation's alkyl chain that are currently identified as very promising candidates for use in a number of state-of-the art processes and applications.

The major foregrounds of this WP were:

- Novel experimental protocol for the effect of water on the CO_2 absorption of ILs.
- Effect of purity of TCM anion based ILs on their CO_2 absorption
- Mixtures of TCM anion based ILs with water, having enhanced CO_2 capture capacity and faster capture kinetics

WP5: Within this WP, Partners NCSRD and IT have firstly elucidated the most appropriate solid substrates for the development of Supported Ionic Liquid Phase absorbents (SILPs). This was implemented by synthesising and testing a variety of nanoporous materials including carbon nanostructures (carbon nanotubes, multi-walled and single-walled, aligned carbon nanotubes), activated carbon, silica based nanoporous materials (mesoporous ordered silicas MCM and SBA, porous glass, aerogel silica) and non-porous silica (pyrogenic silica substrates). Moreover a series of nanoporous membranes including mono-channelled ceramic monoliths with pore sizes of 1, 5, 10 and 70 nm, CVD modified ceramic monoliths with pore size below 1nm, carbon hollow fibers with microporous skin layer and Zeolite Imidazolate Framework membranes have been synthesised and tested as substrates for the development of Supported Ionic Liquid Membranes (SILMs). At a second stage, two methodologies for the modification of the porous substrates and the production of the respective SILPs and SILMs have been examined. Those included the physical imbibition method, where the IL solution or bulk IL is allowed to fill-in the pores of the substrate under vacuum or pressure difference, followed by solvent evaporation and the grafting method (distinguished in the “grafting to” and the “grafting from”) where the Partners have achieved the chemical attachment of the IL on the pore surface, having previously functionalised both the IL and the surface with appropriate chemical entities that could react each other. In the “grafting to” method an alkoxy-silyl functionalised IL was first synthesised and then chemically attached to a hydroxyl functionalised pore surface. In the second approach the alkylation reaction with a chlorosilane was initially performed to attach on the methyl imidazolium ring a chain terminating to an alkoxy-silane entity. The as produced halide IL was firstly attached to the surface followed by the last step of the metathesis reaction (anion exchange) to remove the halide and add the anion of choice for ensuring affinity to CO_2. Testing of the CO_2 and N_2 absorption capacity of SILPs was performed with the gravimetric method (IGA) that in addition provided information on the kinetics of the absorption while the most promising amongst the SILP absorbents were also tested with gas breakthrough curves in fixed beds. The membranes were tested in permeability/selectivity rigs existing at NCSRD applying the Wicke-Kallenbach method of measurement. A hybrid membrane separation fixed be process (HSS Class-1) was developed by Partner N.G.G withing WP8 and installed at NCSRD’s labs that allowed within WP5 the testing of upscaled quantities of the materials. A major conclusion of the overall work was that the grafting method in combination with substrates characterised by well organised porous network with parallel channels (no tortuosity, MCM, SBA) have the potential to produce SILPs and SILMs with fast CO_2 absorption kinetics (high diffusivities and permeances for the SILMs). While this approach is the most promising for membranes it is not quite satisfactory for absorbents mainly due to the inherently limited solubility of CO_2 in physisorbing ILs at low pressures. Here, the contribution of FAU with the development of Inverse Supported ILs (work performed in WP2) was important. Most of the Inverse SILPs produced within WP2 were tested within WP5 by NCSRD and the results were directly compared with SILPs developed with the physical imbibition and grafting methods. In overall within WP5 we have produced and tested more than 20 different SILPs and SILMs. Except from the permeability/selectivity characterisation we have also applied advanced methods such as Raman profiling in the cross section of the SILMs to elucidate the depth of the IL imbibition as well as XRD and Differential Scanning Calorimetry to elucidate the effect of the nanopore confinement on the Physical state of the IL (effect on the T_g, phase changes, liquid crystalline forms, crystallisation, freezing and melting points shift)

As a general conclusion drawn from testing the performance of most of these materials we propose:

1) Inverse SILPs with 40% content of N,N,N-Trimethyl-N-propylammonium prolinate (60% silica) for CO_2 capture achieving a CO_2 absorption capacity of 1.8 mmol/g in a stream of 15 vol.% CO_2 at 1 bar and 40°C.
2) Inverse SILPs with 57% content of [BMIM][Cl], 3% Chitosan (40 % silica) for desulfurization achieving a SO_2 absorption capacity of 1.6 mmol/g and CO_2 absorption capacity of 0.5 mmol/g in a stream of 0.13 vol.% SO_2, 13.2% CO_2 and 11.7% O_2 at 1 bar and 40°C.
3) SILPs developed with the grafting method on activated carbon using the IL [SPMIM][OAc] for CO_2 capture achieving a CO_2 absorption capacity of 3.05 mmol/g in a stream of 0.13 vol.% SO_2, 13.2% CO_2 and 11.7% O_2 at 3 bar and 25°C.
4) A SILM membrane for flue gas desulfurisation developed on ceramic monolith with 10nm pore size using [C_8MIM][TCM] as the IL phase. This type of membrane could be applied in a desulfurisation processes as it exhibited an SO2 permeability of 6000Barrer, a SO_2/CO_2 selectivity of 30 and % recovery of 30%.
5) A SILM membrane for CO_2 separation developed on ceramic monolith with 10nm pore size using [EMIM][TfO] as the IL phase. This type of membrane could be applied in a CO_2/N_2 separation processes as it exhibited an CO_2 permeability of 30Barrer and a CO_2/N_2 selectivity of 40.

The most important results are following described.

The main S&T results of WP5 were:

1) SILPs developed with the grafting method on MCM 41 substrate with pores of 2.3 nm, using ILs of silylated imidazolium cation and PF_6^- anion exhibited CO_2 absorption capacity of 0.19 and 0.313 mmol/g at 1 bar and 35 and 0°C respectively while the ideal sorption CO_2/N_2 selectivities were of the order of 92 and 1043. Using MCM 41 substrate with larger pores of 3.3 nm and the same grafting procedure, the CO_2 absorption capacity was 0.12 and 0.25 mmol/g at 35 and 0°C respectively and the ideal CO_2/N_2 selectivities were of the order of 3 and 32. It should be also noted that the rate of CO_2 absorption in these SILPs developed with the grafting approach was two orders of magnitude higher as compared with SILPs developed with the physical imbibition method using PF_6^- anion ILs. A major conclusion was that with the grafting approach, the pore size must be small enough to ensure complete blocking of the pore entrance to the N_2 molecules. In other words the CO_2/N_2 selectivity is moderate if the pores are not blocked by the IL phase.

2) Comparing between the grafted and physical imbibition methods the following conclusions were drawn. Physical imbibition leads to the formation of SILPs having almost the same CO_2 absorption capacity with those created with the grafting method

and a CO_2/N_2 selectivity which is defined by the performance of the entrapped IL phase. The grafted SILPs have the advantage of fast absorption rate. The main explanation is the orientation of the IL molecules with the cation towards the pore wall and the anion towards the core of the pores. Taking into account that the CO_2 molecules interact strongly with the anions in ILs (PF_6, Tf_2N, TCM, Arg, are the anions we used to synthesise the silylated ILs) we must have the creation of straight diffusion paths inside the pores where CO_2 molecules undergo a hoping mechanism between the anions oriented towards the core of the pores.

3) The SILMs developed with the grafting method exhibited very high CO_2 permeability (500+ Barrer) and satisfactory CO_2/N_2 selectivity of 25. However the reproducibility of these results when trying with ceramic monoliths of other pore sizes (e.g 5 nm instead of 1 nm) and with other anions instead of PF_6 was very poor. We have concluded that there must be a specific relation between the pore size and the molecular size of the IL in order to achieve the oriented attachment of the IL's cations and anions and ensure the blocking of the pore entrance to N_2 molecules. Only two out of the five membranes developed with the grafting method had achieved high CO_2 permeation and satisfactory CO_2/N_2 separation and were those developed with the PF_6 anion silylated IL and the ceramic monoliths of 1nm pore size.

4) Inverse SILPs enclosing ILs with aminoacid anions (taurinate and prolinate) are very efficient CO_2 absorbents and constitute the best materials to be used in a CO_2/N_2 separation process. However they suffer from significant deactivation in the presence of SO_2 with the CO_2 absorption capacity dropping to almost half value compared to the efficiency in a stream containing only CO_2 and N_2.

5) Inverse SILPs enclosing ionogels of [BMIM][CL]/Chitosan are excellent absorbents for SO_2. They present an SO_2 absorption capacity of 1.6mmol/g in a stream of SO_2 0.13 vol.%, CO_2 13.2 vol.%, O_2 11.7% at 1 bar and 40°C and SO_2/CO_2 selectivity of 300+ and could be applied in a pre-treatment desulfurisation step to the above Inverse SILP materials with prolinate and taurinate anions.

6) Despite the good permeation properties of SILM membranes developed with the grafting method using silylated IL with hexafluorophosphate anion (PF_6), we judged that their development is not facile and includes stages of use of polar organic solvent (ACN or toluene) for the grafting reaction to be completed. For that reason we have developed a series of SILMs with the physical imbibition method under vacuum using all series of the TCM anion ionic liquids ([C_nMIM][TCM] with n=2,4,6,8) as well as a couple of new ILs synthesised by IoLiTec during the 3rd period ([EMIM][TfO] and [EMIM][DEP]). We used the 10 nm mono-channeled monoliths as we have found that in the mololiths of smaller pore size (1 nm, 5 nm) the confined IL usually undergoes phase changes and is converted to a liquid crystalline phase having very high viscosity concluding to significant attenuation of the permeance.

7) The experimental campaign with the membranes included two sets of experiments all performed with real mixtures in the Wicke-Kallenbach configuration. In the first set of experiments the membranes were tested with a mixture of CO_2 with N_2 as feed, at CO_2 molar concentrations varying between 0.05 and 0.5 mol/mol and at different temperatures between 25 and 70°C. Moreover the feed pressure varied between 1 and 4 bars. In the second set of experiments the feed stream was composed of SO_2 0.13 vol.%, CO_2 13.2 vol.%, O_2 11.7% and balance N_2 and the experimental campaign included solely alteration in the feed pressure (from 1 to 3 bars) and temperature (from 25 to 70°C).The major output was that the best performing membrane for SO_2/CO_2 separation was the one modified with the IL [C_8MIM][TCM].The best performing membrane for CO_2/N_2 separation was the one modified with the IL [EMIM][TfO].

8) The Ionic Liquid [C_8MIM][TCM] has been successfully used for mending inter-crystalline pores in a ZIF-69, Zeolite Imidazolate Framework membrane. The specific IL was selected since the molecular size did not allow its imbibition into the intra crystalline pores of the ZIF. Moreover the CO_2/N_2 separation efficiency of the IL has significantly contributed to the CO_2/N_2 separation efficiency of the ZIF crystals concluding to a hybrid membrane with performance which was exactly on the upper threshold line of a Robeson plot for CO_2/N_2 separation.

The major foregrounds of this WP were:

- A novel concept of SILP absorbents consisting of IL droplets sleeved by silica nanoparticles.
- SILM membranes prepared by an easily upscalable technique for CO_2/N_2 and SO_2/CO_2 separation.

WP6: Within this WP, Partners NCSRD, IT and FAU have achieved the upscaled synthesis of the most promising of the synthesised ILs and poly-ILs at the highest possible purity and the lower cost and the upscaled development of supported ionic liquids absorbents (SILPs) and membranes (SILMs). A series of ILs, fourteen (14) different structures including two different silylated ILs have been synthesised by Partner IoLiTec (IT) at the kg scale and distributed to the partners for performing their thermophysical/physicochemical, corrosiveness and toxicity characterisation. In parallel, the synthetic procedure of the most promising of these ILs (the [CnMIM][TCM] with n=4,6,8) has been adapted to a state of the art microreaction technology which enabled IoLiTec to produce the selected Ionic Liquids in a continuous flow process in quantities up to 65 kg while meeting the highest quality standards. NCSRD has proceeded with the production of large quantities of porous substrates that could be synthesised with an easily up scalable and controllable process. In this regard the most prominent materials were the carbon nanotube bundles MWCNTs fabricated by Chemical Vapor Deposition (CVD) in powder form using xylene/ferrocene. The initially planned silica aerogels produced by sc-CO_2 extraction have been omitted because of their moderate thermal stability. In regard to the up scaled SILMs, NCSRD selected to use commercially available ceramic (alumina-silica) membranes of half (0.5) meter length and 10 mm OD while Carbon Hollow Fiber membranes had also been produced by pyrolysis and activation of polymeric precursors. The polymeric nascent fibers have been developed in large quantities (10 meters per hour) at NCSRD facilities. The dry/wet phase inversion technique was applied in a large scale spinneret set up using a poly-imide copolymer as precursor. The fragility of the CHFs and the moderate performance of the as derived lab scale SILMs make us to proceed with the upscaled production of SILMs using the commercially available ceramic monoliths of 10 nm pore size. FAU had a significant contribution in the upscaling of SILPs, introducing an environmental benign and facile approach for the development of large quantities of Inverse SILPs using the cheapest amongst the solid substrates (pyrogenic silica) and a variety of ILs including chemisorbing and physisorbing ones and biopolymer/IL ionogels.

The main S&T results of WP6 were:

1) Two TSILs (1-ethyl-3-methylimidazolium lysinate (EMIM Lys) and 1-ethyl-3-methylimidazolium serinate (EMIM Ser)) have been successfully upscaled to amounts of 4kg, while improving the yields in comparison to the small scale synthesis and reducing the amount of solvents used. The synthesis of one of the ILs developed for physical sorption and shown very good co-solvent properties (1-butyl-3-methylimidazolium tricyanomethide (BMIM TCM)) has been successfully upscaled to a 10kg amount without loss of purity and retention of very good yields compared to the small scale synthesis.
2) Two protic ILs 1,8-Diazabicyclo[5.4.0]undec-7-en imidazolide (DBU Im) and Diazabicyclo[5.4.0]undec-7-en pyrazolide (DBU Pyr) can successfully upscaled to 10kg and more using flow and microreactor technology, without loss of purity and retention of very good yields compared to the small scale batch synthesis.
3) Up scaling of the ILs silylation procedure did not required the production of ILs in large quantities. Indeed, amongst the supports that have been developed at large quantities in order to graft the silylated ILs, the carbon nanotubes exhibited satisfactory pore volumes ranging from 1.5 to 2.5cc/g. According to the planned mass of the supports that could be introduced in the fixed beds (2-3 kg) and assuming a complete filling of their pore structure with the silylated IL this gives about 10 kg of the silylated IL at the maximum. The same holds for the Carbon Hollow Fibers (CHFs) that could be used as upscaled supports for the production of SILMs with the grafting from method. In this case however our effort will be to restrict the deposition on the internal microporous layer of the CHFs that has a thickness of some tenths of nanometers and constitutes less than 1/1000 of the mass of the entire carbon CHF. According to the porosity of this ultrathin microporous layer and the required membrane area (0.03 m^2) to be implemented in the hybrid bed absorption/membrane process, the foreseen quantities of silylated ILs that would be needed for the grafting do not surpass the 1 kg. In this context three silylated ILs have been produced by Partner IoLiTech at the kg scale and sent to NCSRD to perform the grafting procedure. These were the 1-methyl-3-(3-triethoxysilylpropyl) imidazolium hexafluorophosphate ([spmim][PF_6^-]), the 1-methyl-3-(3-triethoxysilylpropyl) imidazolium tricyanomethanide ([spmim][$C(CN)_3^-$]) and the 1-methyl-3-(3-triethoxysilylpropyl) imidazolium arginate ([spmim][arg]).
4) The best performing silylated IL (SPMIM PF_6) was further modified by synthesizing the corresponding BTA salt, to optimize viscosity and thermal stability. The necessary up-scaling to an amount of 2 kg was possible without loss of purity (99%) or yield (total of 82% over two steps), which by calculation is required for the treatment of a 0.5 m^2 membrane surface.
5) An economic method to produce large quantities of MWCNT bundles is the CVD process with the use of xylene or benzene as the source of carbon and Ferrocene as the source of metallic catalyst has been developed by Partner NCSRD. This method does not require the previous deposition of the metal catalyst and the development of the nanotubes takes place on the entire surface of the applied substrate. In this way we can develop bundles of MWCNT on the hot walls of the stainless steel tube of the CVD reactor without the need of any special substrate.
6) Carbon hollow fibers (CHFs) as substrates for SILMs have already been developed at the 15cm length. Although the polymeric precursors (co-polyimide hollow fibers) could be produced at a scale of 100 meters per day, there were limitations in the achievable length for the CHFs; limitations that are attributed to the short length of the isothermal zone of the furnaces available in the Lab (NCSRD). Moreover, SILMs developed on the 15cm length CHFs exhibited moderate CO_2/N_2 selectivity and CO_2 permeability (see deliverable 5.7). In this context CHFs were not chosen as the substrates for the upscaled development of SILMs and our efforts focused on the development of SILMs on ceramic nanofiltration and ultrafiltration substrates with the physical imbibition methodology.
7) 10 grams of an inverse SILP with 40% content of N,N,N-Trimethyl-N-propylammonium prolinate (60% silica) for CO_2 capture achieving a CO_2 absorption capacity of 1.8 mmol/g in a stream of 15 vol.% CO_2 at 1 bar and 40^{o}C have been sucesfully synthesised.

8) 10 grams of an inverse SILP with 57% content of [BMIM][Cl], 3% Chitosan (40 % silica) for desulfurization achieving a SO_2 absorption capacity of 1.6 mmol/g and CO_2 absorption capacity of 0.5 mmol/g in a stream of 0.13 vol.% SO_2, 13.2% CO_2 and 11.7% O_2 at 1 bar and 40°C.
9) We have proceeded with the development of upscaled SILMs utilising the direct SILM physical imbibition method with the application of vacuum at the shell side of the ceramic monoliths while the lumen space was filled with the ILs [CnMIM][TCM] with n=4,6,8, [EMIM][DEP] and [EMIM][TfO]. The same device used for the development of the lab scale SILMs was involved with only difference the replacement of the reactor cell with a longer length glass tube.

The major foregrounds of this WP were:

- Microreactor technology successfully applied for the upscaled synthesis of TCM anion based ILs.

WP7: Within this WP, Partners N.C.G and PPC after having reviewed solvent and process improvements in commercial plants, have further proceeded with the optimum design of the Scrubbing/Stripping Pilot Unit incorporating the new MEA/IL solvent and have conducted the Process Engineering and Optimisation study of the Scrubbing/Stripping and Hybrid Separation (HSS) processes.
More specific N.C.G has implemented a comparison of solvents in real terms based on a thorough survey of significant flow sheet improvements that have been published in both the open academic and patent literature for reactive liquid absorption-based CO_2 separation processes. The output of this study was that ionic liquids for CO_2 capture are gaining interest and have great potential due to their unique characteristics, i.e., wide liquid range, thermal stability, negligible vapour pressure, tunable physicochemical character and high CO_2 solubility. In addition, several modifications in the flow-sheeting and solvents of the Scrubbing/Stripping process such as, improved solvent formulation, split flow configuration, stripping with condensate flash steam, absorber intercooling and integrated steam generation have the capacity to enhance the energy efficiency of the CO_2 capture process. For reasons of limited budged and since our major target was to directly compare between the process efficiency using ILs and MEA we have decided not to implement flow sheeting modifications but follow the standard flow-sheeting of the CO_2 capture process with absorption and still columns. Partners N.C.G and PPC continued with the basic design aspects of a MEA absorption process for capturing the CO_2 contained in the flue gas coming from a natural gas thermal power plant at Public Power Corporation (PPC) in Lavrio district. The basic units of the process are the absorption packed tower, the regeneration column for MEA solution and the reboiler. The diameter and height of the absorber column was initially calculated which should be well below the flooding point but also high enough in order sufficient gas to liquid contact and packing wetting to be ensured. The packing height and packing material characteristics were defined. The design of regenerator required the rating of reboiler and the determination of column diameter as well as the number and structural characteristics of the plates. The optimum integrated design for the power plant with an IL based CO_2 scrubber was achieved for the Thermoelectric Plant of our Partner PPC S.A. at Megalopolis (Megalopolis B Unit IV). After changing the site for the installation of the Pilot Unit from an NGCC plant to a coal fired plant we were obliged to perform the simulation studies having the valuable input of our partner PPC that provided data on the steam turbine, the thermodynamic characteristics of the steam, the boiler, the deNOx and fly-ash collection systems, the integrated FGD unit and the characteristics of the fuel (lignite). The model of CO_2 capture from the flue gas via chemical absorption with MEA solvent was based on an ASPEN model with the appropriate existing/preselected properties of chemical substances for the simulation of the process. The simulation took place based on the mass transport rate (rate based process). For the solution of electrolytes the model of Aspen with CHEMISTRY ID MEA was used where the assumption was made that the reactions of ions are in chemical equilibrium. Moreover for the scrubbing and stripping towers we have used model based on the kinetics of the reactions (REACTION ID MEA-REA ABSORBER/STRIPPER), in which, all the reactions are considered in chemical equilibrium, except from those of CO_2 with OH^- and CO_2 with MEA. The capture of CO_2 by a chemisorbing IL [C_2OHmim][Gly] was described by a system of chemical reactions that involve the generation of a zwitterion as is exactly the case with MEA. Taken that the CO_2 emissions of the Power Plant when operating at full load is over 5500 t/day, solely one fraction of the total flue gas emission of the order of 45% was driven to the capture plant. The simulations of the Power Plant have been performed with the use of appropriate software of thermodynamic cycles which used as input the steam abstracted for the operation of the reboiler (derived via the simulations in ASPEN).
For the simulation of the HSS process an efficient model was developed on the g-proms platform that has the capacity to predict the effect of several parameters to the performance of SILM membranes. These included: i) The effect of feed pressure (P) on the permeate mole fraction (Y_p) and on the stage cut in SILMs supported on mono-channelled monoliths for various selectivities (α) and stable feed flow rate and feed mol fraction. ii) Estimation of the driving force across the membrane along a SILM membrane supported on mono-channelled monoliths for various selectivities (α), and constant feed pressure flow rate and molar fraction. iii) The effect of feed pressure (P) on the permeate mole fraction (Y_p) and on the stage cut in a SILM

membrane supported on mono-channelled monoliths for various feed mole fractions (X_f) and constant feed flow rate and selectivity.

Finally the optimum operation conditions of the scrubbing/stripping unit have been defined, taking into account that the initial design was performed for capturing CO_2 from a 5000Nm^3 flue gas stream from an NGCC plant containing 5 vol.% CO_2 while in the real application (due to change of the installation location) the flue gas contained 14 vol. % CO_2. Optimisation of the capture efficiency was achieved by exploiting the design procedure which allowed us to apply up to 50% higher flow rate for the solvent as well as the fact that the wetted parts of the process have been contracted by stainless steel and therefore a change of the solvent content from 20 to 30% was permissible.

The main S&T results of WP7 were:

1) Efficient design of the scrubbing/stripping unit was implemented concluding to accurate dimensioning of the basic components (Scrubber of 0.85m diameter 15 m height and two packing sections of 5 m height. Stripper of 12 m height, 0.7 m diameter with 16 plates appropriately designed and plate spacing of 60 cm. Reboiler with a total heat exchanger surface of 72 m^2). The efficiency of the design was further validated within WP8 during the operation of the Unit where we have achieved the planned CO_2 capture efficiency of 55%.
2) The CO_2 capture process with MEA and MEA/IL (chemisorbing IL) was simulated with the ASPEN plus software for the treatment of 45% of the flue gas from a 300MWe gross power thermoelectric plant (Unit IV) at Megalopolis. The Gate Cycles software was used to simulate the thermoelectric plant which used as input the steam abstracted for the operation of the reboiler (derived via the simulations in ASPEN). The steam is abstracted from the steam turbine at 3.6 bar which is sufficient for the operation of the reboiler ~3 bar, assuming a small pressure drop of 0.5 bar from the point of abstraction to the input of the reboiler. The simulations have showed that with the MEA/IL solvent we can achieve 6% reduction of the specific thermal energy required for the regeneration and respective reduction in the energy consumption for the pumps of the capture unit. Application of the capture system to the coal fired thermoelectric plant at Megalopolis concluded that the net electric power of the plant is reduced by 17.8 MW for the capture with MEA and by 17.0 MW for the capture with MEA/IL as compared to the reference plant. The respective reductions of the net power efficiency were by 2.5 and 2.4%. The use of MEA/IL has as result the improvement of the net power efficiency of the plant with integrated CO_2 capture unit by 26%.
3) We have calculated the maximum permissible flow rate of the solvent and MEA content that would allow us to operate the Pilot Unit at satisfactory capture efficiency, a task which was tricky due to the change of the installation site and the concomitant change of the gas stream conditions (3 times higher CO_2 content). This was 15 tones /h of 30% MEA solution which concluded to a 55% CO_2 capture efficiency.
4) We have performed dynamic simulation and optimisation of the membrane module in the HSS which relied on all mathematical equations describing the dynamic behaviour of Membrane Permeation Modules. The mathematical is a set of Partial Differential and Algebraic Equations (PDAE) developed in the g-proms platform and it can be further applied to investigate two HSS classes in a single flowsheet, pertaining to the CO_2 separation from N_2 and O_2 at CO_2 concentrations between 3% and 15%. With this model we have investigated all cases of membrane operation (Cross Plug Flow, Parallel Plug Flow – Cocurrent – No sweep gas, Parallel Plug Flow – Cocurrent – Sweep gas, Parallel Plug Flow – Countercurrent – Sweep gas).

The major foregrounds of this WP were:

- Design of Pilot Unit for post combustion CO_2 capture.
- Design of a hybrid desulfurisation/CO_2 capture unit of Class 1 (membrane separation followed by fixed bed).

WP8: Within this WP, Partners N.C.G has achieved the construction of the basic components of the Scrubbing/Stripping Pilot Unit according to the design implemented within WP7 and described in deliverable 7.3. Except from the basic design and construction further activities included the calculation of foundation loads for performing the civil engineer study and conclude to the construction of the concrete platform where the large and heavy components of the process were installed, as well as the automation design of the unit to define the control points for keeping a stable solvent level at the bottom of the stripper and scrubber and establish a continuous lean solvent flow to the overflow section of the reboiler. The pipelines size and material of construction was calculated and defined to allow for the required flow rates of flue gas, steam and solvent without significant pressure drop. The automation system was implemented through a PLC unit that controlled the flow of the solvent pumps and steam and three-way valves that allowed return of condensed steam from the outlet of the reboiler to the top of the stripper, receiving as input the liquid levels at the bottom of the scrubber and the overflow section of the reboiler, the flow rates of the lean and rich solvent pumps, the flow rate of the steam and flue gas, the temperature of the flue gas at the scrubber inlet, the temperatures at the inlet and outlet of the plate type heat exchangers of the solvent, the temperature at the bottom and vapor section of the reboiler, the pressure at the top of the stripper and the temperature at several heights of the stripper. The gas composition at the inlet of the scrubber was provided by the Power Plant, while the CO_2 composition at the top of the scrubber was measured by installing a pipeline of 40 mm ID vertically to the scrubber's exhaust and connecting it to an IR CO_2 analyser. It should be noted that due to the sensitivity of the IR analyser to moisture the stream was completely dehumidified and the obtained values on dry basis (14% vol CO_2 at the feed and about 7 % vol CO_2 at the scrubber outlet) where converted to water saturated gas concentration for further calculating the efficiency. The installation and integration of the Pilot Unit to the Power Plant was successfully accomplished and the operation of the unit was performed for three weeks with a solvent composed of 29 Wt.% aqueous MEA (900 kg in 3.1 m^3) and for about 4 weeks with a solvent composed of 27.3 Wt% MEA and 5.77 Wt % Ionic Liquids (65 kg of each of the [C_nMIM][TCM] ILs with n=4,6,8). Partner (PPC) devoted many man months for the continuous (day and night) operation and monitoring of the unit and implemented a Haztop study taking all the required measures for confronting accidental release of the solvent to the environment. The operation of the Pilot Unit provided valuable data on the steam requirement and solvent flow rate to achieve the maximum CO_2 capture efficiency which was no more than 53% in accordance with the efficiency defined in deliverable 7.6. Moreover it was possible to calculate differences in the solvent degradation rate, efficiency and steam requirements using the two solvents and extract conclusions on the beneficial effect of ILs. These results provided valuable input for Partner PPC to perform the Life Cycle assessment of the process, having also the assistance of Partner IoLiTech who provided the energy required for the synthesis of the specific amounts of ILs used in the unit, as well as to report on the required amount of fresh solvent and the effect of contaminants. It is important to note that regarding the latter; deviations were concluded between the results obtained in the scrubbing/stripping device in the lab and the Pilot Unit at Megalopolis (see deliverable 8.3), fact that highlights the importance of performing pilot tests in real environment where the lessons learnt and conclusions are more reliable. The operation of the Pilot Unit provided also valuable input to WP9 allowing the establishment of the Technology Implementation Plan of the IOLICAP project. Connected with the installation and operation of the Pilot Unit was also the testing of the GWD technology developed by Partner NDtech. As soon as the installation of the unit was performed, NDtech has installed the two MFC sensors (one transmitting and one receiving) which were permanently glued on the lower part of the surface of the vessel (scrubbing tower), in order to acquire periodically (quarterly) GEW reflection pictures from the same position and estimate possible future corrosion. Initial (t=0) measurements were acquired at frequencies 10 kHz, 20 kHz, and 30 kHz. GEW reflection images were stored to be compared (subtracted) by future measurements in order to assess possible steel structure alterations.

An additional task implemented by N.C.G within WP8 was the design and construction of a modular HSS unit. This encompassed the smart design and construction of the fixed bed holders and membrane modules so that to make possible the incorporation of small (up to 1g) and large (up to 10g) quantities of Supported IL absorbents in the fixed bed holders and small (39 cm^2) and large (157cm^2) surface area membranes in the membrane modules without the need of any modifications in the gas manifolds, flow controllers, valves and pipelines providing the gas streams to the devices and in the analytical systems (Gas Chromatographs, Gas specific analysers) alreasy existing at the facilities of Partner 1 (NCSRD). The final design was implemented in accordance to the output of the deliverables of WP5 and WP6 which were crucial for the definition of the morphology of the best performing SILPs and SILMs.

The main S&T results of WP8 were:

1) The inclusion of ILs into the solvent formulation leads to slightly slower degradation rate of the amines (1.26 kg/day compared to 1.28kg/day). This can be attributed to the high strength of ILs as solvents that can dissolve part of the insoluble salts formed between the amines and CO_2. The higher degradation rate observed in the lab scale experiments as compared to the pilot unit can be attributed to the higher CO_2 and O_2 contents in the used gas stream as well as to the use of much less amine content and the presence of copper in several parts of the lab-scale device that can cause additional degradation effect due to corrosion. From the experiments in the lab scale it can be concluded that the beneficial effect of ILs diminishes in the presence of high O_2 content. However, this is in contradiction with the output of the experimental campaign in the Pilot Unit where with a 6 col. % Oxygen content the effect of the ILs is still beneficial. The SO_2 and NO_x content in the real flue gas during the operation with the Pilot Unit was very low to extract any reliable conclusions on possible contribution of SO_2 in the degradation of MEA.

2) The most important conclusion is that in physisorbing ILs such as the [OMIM][TCM] used also as component in the solvent formulation of the Pilot Unit there is no competitive effect between SO_2 and CO_2. In fact, the CO_2 absorption capacity of about 0.2 mol/mol obtained in the presence of SO_2 is almost equal with the absorption capacity obtained in single phase CO_2 absorption experiments described in WP4. Therefore, it is expected that the contribution of these ILs on the CO_2 absorption capacity of the solvent in the Pilot Unit is not affected by the presence of trace quantities of SO_2.

3) A common feature with both solvents was that the CO_2 capture efficiency increased with increasing steam supply rates in the reboiler, between 1000 and 1250 kg/hr, then it increased slighter approaching to approximately 55–56% (maximum efficiency)

over the steam supply rate of 1250–1800 kg/hr. Based on the operating data the maximum CO_2 capture performance (more than 55% of CO_2 capture efficiency) at the minimum reboiler heat duty was achieved at steam supply rate of approximately 1320 kg/hr for the solvent (MEA 27.3 %, IL 5.77%) and 1400 kg/hr for the solvent (MEA 29%) at solvent circulation rates of 10000 kg/hr (L/G = 2 l/m^3) or 14000 kg/hr (L/G = 2.8 l/m^3). The respective energy per kg of CO_2 captured is 3700 kJ/kg in the case of the solvent with the IL and 3924 kJ/kg in the case of the solvent with MEA 29 Wt%. As concluded in our recent publications the replacement of part of MEA with a small portion of ILs with tricyanomethanide anion has as result both the improvement of the solvent capture efficiency and the required energy for regeneration.

4) The improvement of the solvent efficiency is attributed to three reasons. Contrary to other ILs, TCM anion ILs exhibit the property of increased capture efficiency when dissolved in water. For instance, [BMIM][TCM] and [OMIM][TCM] absorb 0.093 and 0.07 mol CO_2 per mol IL at 250 mbar (partial pressure of CO_2) and 40°C when fully saturated with water, while the respective performance in their dry state is 0.05 and 0.06 mol CO_2 per mol IL. Moreover, the rate of absorption becomes one order of magnitude higher when the ILs contain significant amounts of water. Taking into account that the isosteric heat of sorption is of the order of 10kJ/mol it can be concluded that the aforementioned capacity of 0.093 and 0.07 mol/mol equals the working capacity (the IL is fully regenerated at the conditions of the reboiler). On the other hand MEA has a working capacity of 0.48-0.15 = 0.33 mol/mol which is about 3 times higher than that of the ILs. Therefore the ILs can have a significant contribution to the sorption capacity of the solvent. Moreover, due to their basic character ILs can act as very efficient proton abstractors contributing to the zwitterion mechanism as strong bases that receive the protons form the unstable carbamate ion leaving secondary amino groups free to bind with more CO_2. The 5.7% decrease of the energy demand for the solvent regeneration is attributed to the portion of the CO_2 captured by the ILs.

5) Experiments have been performed with the HSS unit applying a Class 1 process with a stream of 500ml/min at 3 bar and 40°C using: **CO_2/N_2 separating membranes (SILM CO_2).** Total surface 1570cm^2. **SO_2/CO_2 separating membranes (SILM SO_2).** Total surface 157cm^2. **CO_2/N_2 separating absorbents (Inverse SILPs CO_2).** Mass 25 g, time on stream before desorption 35 minutes. **SO_2/CO_2 separating absorbents (Inverse SILPs SO_2).** Mass 2.2 g, time on stream before desorption 6 hours. The Process gave SO_2 recovery of 99.99% with a purity of 58.33% and CO_2 recovery of 36.7% with purity 98.33%.

The major foregrounds of this WP were:

- A pilot unit for CO_2 capture from 5000 Nm^3/h of flue gas.
- A hybrid desulfurization / CO_2 capture unit of Class 1 (membrane separation followed by fixed bed), with the capacity to accommodate up to 10 g of Inverse SILP absorbents and membranes with a total surface of 157 cm^2.

WP9: Within this WP, Partner NCSRD has organised two outreaching and dissemination activities in order to promote transfer of knowledge at the National, EU and International level and to a multitude of technology end-users as well as other shareholders, third parties and the general public. NCSRD MESL (Dr G. Romanos) took the initiative to organise a European Conference on CCS in 2013. The efforts for communicating the event, sending the mailing lists, invite speakers, invite other European projects, stakeholders and the Industry, preparation of the conference programme, organisation of the venue and preparation of the material for the conference have been shared between Dr. George Romanos (NCSRD/MESL) and Dr Frans Snijkers from the Flemish Institute for Technological Researc (VITO) who was the co-organiser and Host of the Conference. The CCS2013 took place in Antwerp the 28th and 29th of May 2013. We have achieved the participation of five active 7FP EU research projects: CAPSOL, DemoCLoCk, iCap, Innocuous and IOLICAP, funded by the European Commission through FP7, and of two recently funded FP7-CCS projects, OCTAVIUS and CO_2QUEST, as well as of two RFCS-projects ECLAIR and ACCLAIM.

The second event (Final Event) “INTERNATIONAL FORUM ON RECENT DEVELOPMENTS OF CCS IMPLEMENTATION - LEADING THE WAY TO A LOW-CARBON FUTURE” 26TH - 27TH MARCH, 2015 ATHENS, GREECE- ATHENS LEDRA HOTEL, covered all the important aspects of the CCS chain, presenting the latest findings of several European and international projects whose research is critical to the development of safe and economically viable CCS technologies. The event brought together key players in academia, research institutions, industry stakeholders and the European Commission, thus forming a unique knowledge-sharing experience for all.

NCSRD was also in charge to develop the Public relation materials, the Administrative templates and the project related Communication materials as well as the Web site of the IOLICAP. Through these activities the IOLICAP project was presented in EU/South Korea workshop with a view of arranging a twinning arrangement for co-operation between EU H2020 and the South Korean efforts in CCS and moreover in the HORIZON-The EU Research & Innovation Magazine with highlights on the new solvents developed and their potential for application in post-combustion capture and in the European Parliament Magazine (Politics, Policy and People Magazine) Issue 381 16 December 2013.

From the very beginning of the project the members of the consortium (all Partners) have been participated in many events with the target to disseminate the results of the IOLICAP. Thus apart from the Organisation and strong participation in the CCS2013 conference and the 1st CCS Forum we have also conducted more than 40 Oral or Poster presentations in 20 different events related to Ionic Liquids, CCS technologies, and adsorbents and membranes for CO_2 capture.

Extensive collaboration between the groups of the IOLICAP project has already led to 24 published articles in high Impact Factor Journals (Journal of Physical Chemistry C, Journal of Physical Chemistry B, ChemSusChem). We must refer to the excellent collaboration between the modelling groups of NCSRD and Scienomics, and the experimental group of the FAU/SAOT School for the development and validation of accurate force fields having the support of advanced optical techniques that provided the outermost reliable evaluation of physicochemical and thermophysical properties of ILs. We should also refer to the very close collaboration between Iolitec, TU/e, NCSRD/MESL for the implementation of application oriented research regarding the efficiency and properties of IL mixtures with water and finally the complementarity of the Uo Manchester groups and the NCSRD/PCSSL groups towards elucidation of corrosion mechanisms in ILs. It is important that we have also achieved publications in high Impact Factor Journals of High Industrial Interest (I&E Chemistry Research, Chemical Engineering Journal, Journal of Chemical & Engineering Data).

Within WP9, the Partners have proceeded with the definition of the main exploitable results during the meetings in Erlangen (30 month meeting) and in Athens (36 months meeting). As preparation, the Project Partners described individually their insights in the exploitable results. At a further step the commercialisation aspects of the main exploitable foreground were defined which included:

- Further R&D activity and/or collaboration needs for exploitation (and which risks are implied)
- IP-related aspects
- Customer detection (focus on factors that affect purchasing decisions)
- Features of the target market (size, growth rate, share that the technology/product could reach, driving factors likely to change the market, legal, technical and commercial barriers, and other technologies likely to emerge in the near future…)
- Positioning (how the company entitled to the technology exploitation is positioned or should be positioned in the market).

Having these data at hand the exploitation team of the IOLICAP project proceeded with the definition of risks and main issues related to the project's exploitation success and provided recommendations on how to monitor and solve most of the issues.

In parallel, potential issues regarding IPR have been discussed and agreed.

Priority Maps were then constructed that allowed for the definition of the foreground closer to commercialization amongst the 16 exploitable foregrounds of the Project. This was "A solvent formulation for CO_2 capture-A new solvent consisting of a mixture of TCM anion based Ionic Liquids and MEA".

According to this evaluation Partner 4 (IT) has prepared the following an Exploitation Plan for the foreground describing:

I. The Innovativeness introduced compared to already existing Products/Services.
II. The Unique Selling Point (competitive advantages).
III. The Product/Service Market Size.
IV. The Market Trends/Public Acceptance
V. The Product/Service Positioning
VI. The Legal or normative or ethical requirements (need for authorisations, compliance to standards, norms, etc.)

<u>The main output of WP9 was:</u>

1) Execution of two communication events on CCS attracting a wide audience from the academic, industrial and public sector. In total 200+ people participated in these conferences.
2) Iolicap's web site.
3) Public Relation Material, Administrative Templates and project related communication material.
4) Participation in more than 20 International events on CCS, Ionic Liquids and Materials with more than 40 oral or poster presentations.
5) 24 Publications in high impact factor Scientific Journals (amongst them 4 publications in Journals of high Industrial Interest).
6) Update of the dissemination exploitation plan and establishment of the Technology implementation plan based on the input of all the Partners.

WP10: Within this WP, the project Coordinator was responsible for:

- Representing the Consortium towards the EU.
- Ensuring a smooth flow of information and distributing all relevant communications from the Commission.
- The administrative management of the project, which included the distribution of the EU financial contribution as well as the periodic financial reporting.
- The day-to-day overall monitoring and coordination of the project.
- Monitoring the performances of partners against contractual obligations.

- The updating of the work plan following the General Assembly's decisions.

For the management of the project the Project Coordinator was supported by the Work Package leaders. The coordination support team was in close contact during the whole project.

In month 9 the Project Management and Quality Assurance Plan was delivered dealing with the project management of the IOLICAP as well as with two very important aspects: the quality assurance and the risk management. The project's management structure and roles were also reviewed. The Quality management procedures have been defined in relation to the main deliverables of the project. In the area of risk management, the risk management methodology was described, along with the main risks foreseen at the end of the first year of the project. The risks have been classified as general management risks (applicable to most collaborative projects), but also as more specific technical risks related to the technical work carried out by IOLICAP. Strategies for identifying the risks and contingency plans aiming at minimizing the potential impact of these risks have also been defined.

During the second period Amendment No2 of the IOLICAP was implemented regarding the addition of Scienomics GmbH as third party to the Beneficiary Scienomics Sarl.

Main managerial task of the project's Coordinator for the third period was to update the work plan after the Amendments No 3 and No 4 regarding the extension of the project's period from 36 to 48 months (Amendment No 4) and from 48 to 51 months (Amendment No 4). Before that, the Project Coordinator had proposed both Amendments to the General Assembly of Partners, the decision making body of this Consortium, which decided positively on both issues. The signed Amendments No 3 and No 4 and the corresponding Annex I were uploaded to the file manager of the IOLICAP website to facilitate the file sharing among partners. The coordinator has informed all the WP leaders on the major changes in Annex I.

Major risks were identified during the third period mainly related to the delay in the installation and operation of the Pilot Unit, activity which was connected with most of the deliverables of WP8, one deliverable of WP3 and two deliverables of WP9.

This period was decisive for the implementation of the work and tasks within WP8, and the related deliverables of other WPs such as D 3.8 regarding the comparison of corrosion evaluation in the laboratory and pilot plant and deliverables D 9.4 and 9.5 regarding the initial life cycle assessment of the developed technologies and the plan for exploitation and dissemination of the results obtained from the operation of the Pilot Plant with MEA and with MEA+ILs solvents. As soon as the decision for IOLICAP extension was signed by EU and the respective Annex I accepted, the Coordinator together with Partners, 7 (PPC), 8 (N.C.G.), 10 (NDTec), 5 (UM), e.g. those involved in the tasks and deliverables related to the construction, installation and operation of the pilot unit, have established a work plan of the period setting target dates for the implementation of certain tasks which were:

1) 15/05/2015. Construction of the Scrubber, Stripper and Reboiler to have been completed and the tower's internals to have been defined and purchased.
2) 20/05/2015. Official decision (signed and stamped) regarding the definition of the Power Plant of Partner 7 that will be retrofitted by the CO2 capture Pilot Unit and official permission for starting works at the Power Plant's premises.
3) 30/05/2015. Preparative work on the scrubbing and stripping towers regarding the attachment of pipelines before their lifting and installation to have been completed.
4) 15/06/2015. Transfer of the major components (Scrubber, Stripper and Reboiler) to the Power Plant.
5) 15/07/2015. The engineering studies for the general layout of the pilot unit, the static designs of the cement support platform, the statics calculations and the designs of the basic components are all completed and starting of excavation works to prepare the terrace for the development of the cement platform that will support the Pilot Unit and the Reboiler's base.
6) 01/09/2015. The scrubbing/stripping tower and the reboiler are installed on place.
7) 30/10/2015. The Pilot Unit is completed. The pipe lines for bringing the flue gas to the boiler and the steam to the reboiler are assembled.
8) 30/11/2015. The priming with deionised water is completed and the first hydraulic and leak tests are performed. Leaks are fixed.
9) 7/12/2015. Partner 10 (NDTec) to have installed two MFC sensors (one transmitting and one receiving) on the lower part of the scrubber, in order to acquire periodically (quarterly) GEW reflection pictures from the same position and estimate possible future corrosion.
10) 15/12/2015. Operation with solvents.

During all this period the Coordinator and the other Partners were informed on the evolution of the work through informal meetings and everyday communication via emails and skype.

Description of the potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and the exploitation of results. (10 Pages)

The expected impacts for the call ENERGY.2011.5.1-1 were two (2):

1. The significant reduction of the energy intensity of the capture process for power plants or other energy-intensive industries.
2. The substantial decrease of the environmental impact and the cost of capture.

Although the terms “significant” and “substantial” are not definite for the extent of improvements needed in the several “components” of a post combustion capture process (from the solvent properties to the design of the towers and the ways of steam exploitation), the IOLICAP project did not relied on already examined, plant specific, and not so efficient formulations (mixing of amines, MDEA, PZ, corrosion inhibitors, degradation inhibitors). It rather started form the basis of a completely new class of solvents (Room Temperature Ionic Liquids RTILs), which however had already showed very promising results for their application in post combustion CO_2 capture. Moreover, RTILs offer the opportunity to be continuously improved due to their chemical tuneability and for this reason they hold a great promise to revolutionize many industrial processes including post-combustion capture form any kind of power plant or industrial sector. In this context the probability to successfully develop a few task specific ionic liquids with improved scrubbing/stripping performance out of the dozens that have been examined (with the aid of modelling) in the course of this project was thoroughly enhanced.

Within the 51 months of IOLICAP, 30+ ILs has been synthesised and characterised and their CO_2 capture performance has been evaluated.

Three promising solvent formulations have been defined.

Solvent 1, (DEA 7%, MDEA 6.9%, TCM- ILs 6.9% (v/v)) had similar performance with 20-30% DEA.

Solvent 2, (MDEA 7.77%, TCM anion ILs 7.76%) had better performance compared to MDEA 20%.

Solvent 3, ([emim][Lys]/[Ser] 8.5%, TCM anion ILs 10%) exhibited 93% of the capture performance of DEA 20%. These results are very promising.

Before claiming the possibility to apply these solvents and refer to their potential impacts, it was essential to investigate several other issues. Amongst them were: Corrosivity, stability (in oxygen and acidic gases) and toxicity.

Corrosion tests revealed that, immersion of MS in the amine-functionalised ILs [emim][Lys] and [emim][Ser] results in the dissolution of metal over the macroscopic mild steel surface. The aggressive behaviour of these amino acid-based ILs and their corrosivity may significantly impair their application for post-combustion CO_2 capture. However we must note that Solvent 3 contains only 8.5% of these ILs and 10% of [TCM] anion ILs, the latter being not corrosive, neither in their pristine state nor in mixtures with water. Comparing with the examined Corrosion Rates (MPY) of typical amines: 30% Wt MEA=32>50% Wt DEA=25>15% Wt MEA=13>20% Wt DEA=8>50% Wt MDEA=3 it can be foreseen that the 8.5% composition will trigger very slow corrosion rates. The major impact from the use of Solvent 3 (the same holds for Solvent 1 and Solvent 2) will be the possibility to use cheaper alloys for the construction of the capture plant which can reduce the capital cost by a factor of 5. Moreover amines do gradually evaporate and degrade. The annual emission of amines to the air (due to slippage) for a 400MW plant can vary from 40-160 tonnes and some of them are proved to be toxic and even carcinogenic, especially the degradation by products like Nitrosamines. It is also estimated that the amount of degraded amine per year for a 400MW plant can be up to 690 tones. Replacement with the less volatile (Solvent 3) will have a tremendous environmental impact. 40 tonnes of amine slippage per year means a vapour concentration of below 1ppm in the stream escaping the scrubber. Huge amounts of energy for cooling water in condensers are required to achieve this slow slippage rate. This huge energy expense will be avoided due to the non-volatility of [emim][Lys]/[Ser].

In the course of the IOLICAP project we had also the opportunity to compare the performance of the Pilot Unit with a new solvent (Solvent 2) composed of 27.3 Wt% MEA and 5.77 Wt% TCM anion ILs, and the conventional MEA 29 Wt% (Solvent 1) and we have provided valid data for significant impact in many aspects of the process including the degradation rate, the capture performance, the regeneration efficiency, the corrosiveness and the toxicity.

Table 1: Comparison of the capture efficiency and cost between the conventional solvent 1 and the IOLICAP solvent 2.

	Total amount of solvent (ton)	*Total amount of active chemical (ton)*	*Capture Efficiency %*	*Energy demand (MJ/kg CO_2)*	*Degradation rate kg/day*	*Corrosiveness*	*Toxicity MDC (g/l) / IC-50 (g/l)*	*Cost €/ton (metric)*
Solvent 1 (MEA 29Wt. %)	*3.1*	*0.9*	*55*	*3.93*	*1.28*		*1.577/1.315*	*2570*

Solvent 2	*3.1*		*55*	*3.7*	*1.26*		*5.704/4.447*	
MEA (27.3%)		*0.846*						*2570*
[BMIM][TCM] (1.93%)		*0.06*					*0.537*	*3500*
[HMIM][TCM] (2.1%)		*0.065*					*0.19*	*4000*
[OMIM][TCM] (2.1%)		*0.065*					*0.1*	*4500*

Cost of Solvents.
Cost of solvent 1:
Initial Cost: 2313€. Cost demand per year: 1201€
Cost of Solvent 2 (IOLICAP):
Initial Cost: 3794.2€. Cost demand per year: 1182€
It needs 30 years of operation to cover the excess cost from the use of Ionic Liquids. This is due to the lower degradation rate of Solvent 2.

Energy consumption for the synthesis of ILs and MEA.
Solvent 1 MEA = 3.13kg CO2/kg MEA, 6.95kWh/kg MEA, 6255kW
Solvent 2 MEA 5881kW
[BMIM][TCM]=642KW
[HMIM][TCM]=400KW
[OMIM][TCM]=478KW
Solvent 2 costs 1146kW more to be produced.
It needs 22 years of operation to cover the excess energy costs from the synthesis of Ionic Liquids. This is due to the lower degradation rate of Solvent 2.

Energy saving from the capture.
Solvent 1: 26035 GJ/year for regeneration of solvent
Solvent 2: 24511 GJ/year for regeneration of solvent
About 1524 GJ of energy saving per year.

Toxicity and corrosiveness.
The new solvent is 3.5 times less toxic and 2 times less corrosive compared to MEA 29 Wt%. Corrosiveness as evaluated with weight loss measurements and surface characterisation of corrosion products on SS 304 and Mild Steel.

Ionic Liquids related Impacts
The development and application of advanced techniques, to evaluate thermophysical and physicochemical properties with the highest possible accuracy have a major impact towards the short-term application of the ILs in industrial scale since, knowledge of these properties is needed to be implemented in process simulators to reduce uncertainty in industrial application and to validate force fields through molecular simulation in order to be able in the future to predict thermophysical and physicochemical properties and identify structure-property relationships: In the absence of such ability, selection of an appropriate IL for a particular separation can become a matter of trial and error.
The above cross-cutting issues generate cross-cutting needs that the IOLICAP project has satisfied. These included:

- Knowledge of thermophysical and chemical properties
- Measure properties. Among the bulk-fluid properties that have been measured were: density, interfacial tension, heat capacity, stability at elevated temperature, viscosity, diffusion coefficients, conductivity, effect of contaminants, corrosiveness, solubilities in water and other solvents, vapor-liquid equilibria, properties of mixtures of ionic liquids.
- Development of predictive models as equations of state.
- Prediction of thermophysical and chemical properties and identification of structure-property relationships.
- Development of correlations based on structure to predict properties of new ILs
- Validation of computational chemistry models.
- Public web-based database: Much industrial research is proprietary, and neither successes nor failures are publicized
- Toxicity. The question of toxicity have been approached by comparing the effect of ILs and solvent formulations containing ILs on the photosynthetic efficiency of green algae.

- Cost of production. Cost of production has been reduced based on the application of alternative synthetic strategies to synthesize halide free ionic liquids (Purification from halides has a major impact on the cost) and through the adaptation of the microreactor technology. Moreover, the application of HSS technologies applying SILPS and SILMS is expected to considerably reduce the amount of IL needed for a certain application due to the high surface area of the involved supports.

European dimension
The European dimension of IOLICAP is signified in technical terms, in terms of developing a trans-national pool of expertise and also from the expected economic benefits resulting from the diffusion of results across complementary business and geographical sectors. The involvement of SMEs together with the multinational character of the partnership is consistent with the spirit of European Cohesion makes a contribution towards social and economic convergence.

Employment, education, training and working conditions
Due to the nature of the IOLICAP objectives, there was a significant transfer of knowledge and know-how between the partners. As a result, all participants enhanced their skills and their expertise. Dissemination activities ensured further education and training for other researchers and students. The process and chemical engineers as well as the chemists of the participating power plant have get familiar with the basic aspects of Solvent chemical absorption and membrane technology in order to put in practice and operate the developed process. At the same time, the research staff of the academic partners had the opportunity to broaden their scientific interests and gain experience in dealing with issues of industrial significance. Apart from the individual level, the results of the project will produce in general new opportunities in high skill jobs performed by new service sectors and SME's, which specialize in Ionic Liquid synthesis and membrane development and operation for gas separations. Such companies could be placed anywhere in Europe, facilitating in this way technological co-operation and pan-European transfer of skills and expertise. Thus, significant technology transfer to less technologically advanced EU regions can be achieved. As far as safety is concerned, an aspect of top priority for the industrial partners, the outcome of IOLICAP induced significant improvements in the working conditions of the employees carrying out the novel process. The new technology is cleaner and practically less maintenance is needed, resulting in a friendlier and safer working environment.

Quality of life, health and safety of the citizens
The novel solvents and improved processes based on membrane technology resulting from IOLICAP, will definitely influence both health and quality of life for all citizens in many ways. Moving towards a cleaner technology can and will promote the efforts for fighting air pollution and greenhouse effect emissions, which is nowadays a crucial issue worldwide. It will be possible to directly protect the public health, by minimizing the pollution sources which eventually cause all kinds of undesirable symptoms that are induced by prolonged exposure to air of reduced quality. This is very important for people that suffer from, for example, respiratory or heart diseases, but also for citizens who often have to limit their outdoor activities during times of heavy pollution. Quality of life will be objectively enhanced not only in terms of physical wellbeing, but also in terms of social prosperity. The significant energy savings induced by the new technology under development, highlight the added value of the process and the obtained products, a feature that will contribute to the strengthening of the financial status of the user groups that will take advantage of it.

Main dissemination activities and exploitation of the results.
Experimentation for 2 months with the CO_2 capture Pilot Unit at the coal fired thermoelectric Power Plant at Megalopolis (Power Plant B Unit IV) has provided valuable input regarding the operability of the process, the better energy and capture efficiency with the new solvent (mixture of ILs with MEA), as well as the lower degradation rate of the new solvent. Other benefits of the new solvent formulation containing MEA and tricyanomethanide anion ILs such as the lower eco-toxicity and the less corrosiveness as compared to the conventional MEA 20 Wt.% were already concluded via the work performed in WP3 and WP2.

It is noteworthy that we have finally achieved to get valuable input from the operation of the Pilot Unit and define benefits from the use of the new solvent, despite that the unit was initially designed for a CO_2 feed of 5 v. % in 5000Nm^3/h and a targeted capture efficiency of 80% (Integration with a NGCC Plant was initially planned, see also deliverable 7.3).

The transfer from an NGCC plant to a coal fired thermoelectric plant obliged us to operate at much higher CO_2 loading in the flue gas (5000Nm^3/h, 14 v.% CO_2). By increasing the MEA content from the 20 Wt. % (based on which the initial design was implemented) to the 29 Wt. % level and the solvent circulation rate from 10 to 14 tonnes/h we have achieved a capture efficiency of 55%. Although the efficiency was lower than the initial target (55% vs 80%) it corresponded to 18.15 tons of captured CO_2 per day instead of 9.4 ton/day which is almost double amount of CO_2 captured per day with 45% more solvent.

This was mainly attributed to the significant increase of the solvent flow rate that was permissible since the design of the scrubbing tower was implemented with a liquid rate which could be 50% greater than the minimum required (see deliverable 7.3). Moreover the use of Stainless Steel in all the wetted parts and equipment of the Pilot Plant allowed us to increase the concentration of the solvent without facing corrosion problems.

As described in Deliverable 9.4 (Implementation plan), the procedure for defining which of the exploitable foregrounds of the project are closer to commercialization (amongst the 16 exploitable foregrounds) has resulted to the definition of the new solvent based on the mixture of MEA with the tricyanomethanide anion ILs.

From the technical point of view and based on the experimental results from the Lab and the Pilot Unit operation, it was possible to demonstrate that the technology developed during this project shows in summary similar or better technical performance if compared to other existing CO_2-separation techniques. This does mean explicitly that mixtures of (monomeric) ionic liquids with mono-ethanol amine (MEA) and/or di-ethanol-amine (DEA) are showing a similar performance as neat MEA and/or DEA, marking the actual standard. Especially, solvents with low content of TCM anion ILs (below 7%) and amine content which is lower than the usually applied (20-25% instead of 30%) show similar capture efficiency with the standard 30% MEA solvent. Moreover, benefits of the IL-based technology developed in the project are:

- Having a very low vapor pressure (no odor, no escape to the atmosphere),
- mixtures of TCM anion based ILs with water, having enhanced CO_2 capture capacity and faster capture kinetics than the neat IL phase. This is important since in most of the cases with ILs the presence of water degrades their CO_2 capture efficiency,
- less corrosive to typical materials. TCM anion based ILs with long alkyl chains could even act as corrosion inhibitors for mild steel. (beneficiary for the process design),
- CO_2 capture capacity and rate of TCM anion ILs is not affected by the corrosion products and corrosion inhibitors,
- and easier to regenerate (see also D8.5, chemical vs. physical sorption).

Nevertheless, ionic liquids are – even if produced on an industrial scale – nearly two magnitudes more expensive to produce than normal amines: In a model calculation we estimated the production costs per metric ton ranging from 2500 € (under very optimistic assumptions of streamlining processes and drastic reduction of costs for the starting materials) up to 10000 € (2.5 – 10 €/kg), while the same cost for one ton MEA are in the range of 90 € per metric ton.

If the total costs of ownership are brought into considerations, it has to be taken into account that the energy consumption for the regeneration of ionic liquids is lower (3.93 GJ/ton CO2 vs. 3.7 GJ/ton in the case of our solvent, chemical vs. hybrid chemical/physical sorption-desorption, see deliverable 8.5). This does mean that using a faster regeneration process is leading to smaller amount of ionic liquid needed for the whole process. Thus, the overall costs per ton of captured CO_2 can be comparable to those, using current state-of-the-art-technologies.

The overall technology has reached so far a technology readiness level of 6 ("technology demonstrated in relevant environment"). In terms of the technology itself the results from our partners demonstrated in the lab and in the pilot plant indicated clearly that the CO_2-capture using ionic liquids is in principle possible.

To transfer this promising technology at the commercial level the following aspects have to be fulfilled:

a) TRL 7: "System prototype demonstration in operational environment"
b) TRL 8: "System complete and qualified"
c) TRL 9: "Actual system proven in operational environment"

-To transfer the existing IOLICAP-technology to a marketable process, it is essential to collect more data concerning the durability of the plant in particular of the used materials (metals, seals etc.) to calculate the costs per ton of captured CO_2 more accurately.

As described in Annex I, the proposed capture process with the new IL solvent should be demonstrated via 2000+ hours of piloting operation. In the project we have achieved solely 480 hours of continuous operation with MEA 29% solvent and 700 hours of continuous operation with the MEA+ILs (MEA 27.3 %, IL 5.77%) solvent. Therefore, the partners involved with the new solvent technology, the operation and maintenance of the Pilot Unit and finally the analysis of the gas streams and degradation products of the solvents (Partner 1, Partner 4, Partner 7 and Partner 8) should agree to implement the continuous operation of the Unit for at least 6 months after the end of the project at their own cost so that the necessary data are collected for further exploitation.

-Solvent slip to the atmosphere should be detected and quantitated.

As described in Deliverable 8.5, solvent slip to the atmosphere was impossible to be detected due to the absence of a detector or device for collecting and analyze amine at the effluent streams of the scrubber and stripper and due to the fact that the flue gas at the inlet of the scrubber was at 75°C and saturated with water. Therefore, we had condensation of significant amounts of water inside the scrubber which constituted the calculations very complex.

In this context what is needed is a cooler and dehumidifier in the flue gas stream just before its feed to the scrubbing column and a system to collect and analyze condensed water from the top of the scrubber and stripper. These activities would add further cost to the involved Partners who have to decide if it is worthy to cover it towards the possibility of a commercial exploitation of both the new solvent and the Pilot Unit.

A key aspect related with the above could be also to design a more efficient regeneration procedure, reducing the net need of ionic liquid in the process. It has to be kept in mind that in closed process loop the ionic liquid shows theoretically no leaching.

-Independently, for successful technology implementation IOLITEC has to work on production processes to reduce the costs of relevant ionic liquids, being the core component of the overall process.

Although the cost for the production of the ILs used in the new solvent formulation have been calculated under very optimistic assumptions of streamlining processes and drastic reduction of costs for the starting materials, the cost gap between ILs and amines remains as much as two orders of magnitude.

It is essential for IOLITEC to redesign the model of calculation taking into account an important foreground of this project which was: "There is no effect of the purity of TCM anion based ILs on their CO_2 absorption capacity"-"CO_2 capture capacity and rate of TCM anion ILs is not affected by the corrosion products and corrosion inhibitors". Therefore, energy intensive stages of the production process can be omitted, especially those intending the refining of the ILs after their bulk synthesis.

-Maybe an important key aspect that should be taken into account if the total costs of ownership are calculated is that CO_2 can be used to form other products: E.g. in the so called "Dream Reaction", CO_2 is used for the production of polyurethanes (without using ionic liquids).

Furthermore, IOLITEC is currently involved in R&D-projects in which CO_2 is transferred (electro-) catalytically into other products, while in another one CO_2 is used to form methane using the so-called Sabatier-process. This does mean by implementing the IOLICAP-technology, CO_2 is already in a solvent-environment, which enables a follow-up catalytic synthesis to other products such as methane, organic acids, or even other organic building blocks. For a broad exploitation of the developed technology strategic partners, in particular from CO_2-generating industries, are of great importance.

-MSDS of the Ionic Liquids.

As it is the case with most of the amines intended for use in CO_2 capture processes (MEA, DEA, MDEA) the ILs with tricyanomethanide (TCM) anions should be registered in the European Chemicals Agency (http://echa.europa.eu/) acquiring a full registration type (substance registered dossier).

Although an MSDS of the three ILs synthesized by IOLITEC and used in the Pilot Unit already exists, the hazard statements are not defined since the ILs are not yet fully tested.

Despite that we have already implemented eco-toxicity tests there is a lot of work needed towards the commercial application of these ILs in the CO_2 capture process.

These include:

1) Classification Labelling and PBT assessment (GHS, DSD-DPD, PBT).
2) Manufacture use and exposure (Life Cycle description, Uses advised against, Exposure scenarios; exposure and risk assessment).
3) Physical Properties.
4) Environmental fate & pathways (Stability, Biodegradation, Bioaccumulation, Transport and Distribution, Environmental data)
5) Ecotoxicological Information (Aquatic toxicity, sediment toxicity, Terrestrial toxicity)
6) Toxicological Information (Toxico-kinetics, acute toxicity, Irritation/corrosion, sensitization…)
7) Guidance on safe use.
8) Assessment Reports.

Two important findings regarding the ecotoxicity and corrosiveness of these ILs were the following:

-While the pure substances were 2-3 times more ecotoxic compared to MEA and DEA, the aqueous mixtures of ILs with amine at IL contents up to 7 Wt.% were less toxic than the MEA and DEA 30% solvents (see deliverable 2.9).

-The new solvent was 2 times less corrosive than the conventional MEA 30% solvent. This was confirmed *via* mass loss data and *via* examination of the surface of mild steel specimens with EDX and Raman after immersion of the specimens in the solvents at 100°C for 5-6 days. In the case of the solvent composed of MEA and ILs no corrosion products were detected while in the case of aqueous the primary corrosion product was identified as α-FeOOH (goethite) with high accuracy. In the case of the amines, the leaching of ferrous ions took place that were rapidly oxidized to ferric ions in the presence of oxygen and both act as catalysts for the conversion of amines to imines and their further oxidation to ammonia and aldehydes.

The following table includes the major benefits of the new solvent as compared to conventional amines. These can be used as the basis for the establishment of our further dissemination and exploitation strategy. In parallel key recommendations for improvement of the results and the necessity for further work are given with the target to accelerate the commercialization of the new solvents.

	29% MEA solvent	Our Solvent.	Key Recommendations
% CO_2 capture efficiency.	55	55	Tests to be performed for prolonged periods with higher IL content from 6 to 10%.
Energy Efficiency. GJ/ton CO_2 for regeneration	3.93	3.7	Tests to be performed for prolonged periods with higher IL content from 6 to 10% and lower MEA content (from 27 to 20%)
Degradation rate. Kg/day	1.28	1.26	Tests to be performed for prolonged periods of at least 12-months. Analysis of degradation products.
Corrosiveness. Corrosion rate at the stripper overhead μm/year)	500-600	250-300, from lab scale experiments	Tests to be performed for prolonged periods of at least 12-months. Corrosion tests on stainless steel instead of mild steel are required.
Toxicity. MDC of cyanobacteria g/L	1.577	5.704	Toxicity, full LCA is required. Substances should be registered in the European Chemicals Agency.
Slip flow of amines (MEA) to the atmosphere. for a Large Demonstration Unit (tons/year)	90	unknown	Potentially zero for ILs. However, the effect of ILs on the slip flow and escape rate of amines should be defined. Modifications are needed in the Pilot Unit to implement this.
Cost of the solvent in € (3.1 tons). / Cost demand per year for replenishment (€)	2312/1201	3794/1182	Examine further reduction in the cost of IL, especially if refining after the synthesis is not required.

The website of the project is: http://www.iolicap.eu/