CO2QUEST Newsletter

Autumn 2013

CO_2QUEST

Impact of the Quality of CO_2 on Storage and Transport

Introduction

Welcome to the first edition of the EU FP7-funded-project CO2QUEST newsletter, highlighting the most recent technical developments since the project's commencement in March 2013. The CO2QUEST consortium, led by Prof. Haroun Mahgerefteh at University College London (UCL, UK) comprises 9 other partners: Bundesanstalt für Geowissenschaften und Rohstoffe (BGR, Germany), Uppsala University (UU, Sweden), Dalian University of Technology (DUT, PR China), Environmental & Water Resources Engineering Ltd. (EWRE, Israel), Imperial College London (ICL, London), Institut National de l'Environnement Industriel et des Risques (INERIS, France), National Centre for Scientific Research 'Demokritos' (NCSRD, Greece), Onderzoekscentrum voor Aanwending van Staal (OCAS, Belgium), and the University of Leeds (UoL, UK).

CO2QUEST addresses the fundamentally important issues regarding the impact of the typical impurities in the gas or dense-phase CO_2 stream captured from fossil fuel power plants on its safe and economic transportation and storage. The above involves the determination of the important CO_2 mixtures that have the most profound impact on the pipeline pressure drop, compressor power requirements, pipeline propensity to ductile and brittle facture propagation, corrosion of the pipeline and wellbore materials, geochemical interactions within the wellbore and storage site, and the ensuing health and environmental hazards. Based upon a cost/benefit analysis and whole system approach, the results will in turn be used to provide recommendations for tolerance levels, mixing protocols and control measures for pipeline networks and storage infrastructure.

Project Partners

University College London, UK

Bundesanstalt fur Geowissenschaften und Rohstoffe, Germany

Uppsala Universitet, Sweden

Dalian University of Technology, China

Environmental & Water Resources Engineering Ltd., Israel

ICL, UK

Institut National de l'Environnement Industriel et des Risques, France

Demokritos, National Research Centre for Physical Sciences, Greece

Onderzoekscentrum voor Aanwending van Staal, Belgium

University of Leeds, UK

CanmetENERGY, Canada

Pressure Drop, Compressor Requirement and Fracture Behaviour

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University College London, UK

UCL is developing steady-state and transient flow CFD models for pipeline networks to study the impact of impurities in the CO_2 stream on the flow behaviour during normal operation and pipeline failure. A secondary important extension of this work is the development of fluid-structure interaction models for simulating brittle and ductile fracture behaviour for CO2 pipelines containing different types of impurities.

Non-isothermal Steady State Flow Modelling

Minimising the pressure drop and avoiding two-phase flows in CO_2 pipeline networks are essential for reducing compressor power requirements. This is critically important given that the compression penalty for CO_2 capture from coal-fired power plants is estimated to be as high as 12% [1]. To evaluate the impact of CO_2 impurities on compressor requirements and pressure drop in pipelines, UCL is applying a previously developed computer model for the calculation of one-dimensional transient compressible multiphase flows in pipes. This model accounts for both flow and phase-dependent viscous friction, and heat transfer between the transported fluid and the pipeline environment [2-5]. The analysis of the steady-state pressure drop in pipelines will be performed for CO_2 mixtures with impurities as identified by other project outputs. As an outcome of this study, the impurities having the most adverse impact on the CO_2 pipeline transport will be identified. Also, recommendations will be made for the pipeline hydraulic resistance calculations in the subsequent CO_2 transport network optimisation studies.

Pipeline fracture modelling

Running or propagating fractures are by far the most catastrophic type of pipeline failure. As such, it is highly desirable to design pipelines with sufficiently high fracture toughness so that when a defect reaches a critical size, the result is a leak rather than a long running fracture. The Battelle Two Curve methodology [6] has been by far the most common method employed for determining the likelihood of ductile fracture propagation in pressurised pipelines. However, this method employs over-simplistic decompression models where the impact of pipe-wall heat transfer and the effects of friction on the fluid decompression behaviour are ignored [7].

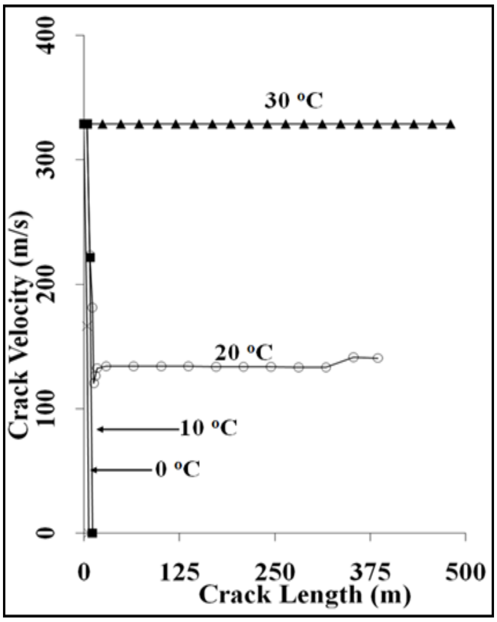

Figure 1. Crack velocity plotted against crack length for a pre-combustion CO_2 stream pipeline at different starting temperatures (Mahgerefteh and Brown, 2012).

Recently, UCL has developed a fully coupled Fluid /Structure Fracture Model (FSFM) [3, 8, 9] which for the first time allows the quantitative prediction of a pipeline's propensity to long running fractures in the form of the variation of crack length with crack velocity and ultimately the crack arrest length (See Figure 1). In the first implementation of the FSFM, the fracture dynamics were modelled using an empirical correlation built upon fracture tests for pipelines containing air. In the CO2QUEST project, the FSFM will be further developed by coupling the UCL outflow model, which has been validated against small-scale and large-scale CO_2 pipeline decompression data [10, 11] obtained in the CO2PipeHaz FP7 project, with more advanced fracture mechanics correlations developed by the partner OCAS based upon the material testing data for steel grades relevant to CO_2 pipeline transportation.

Critical Processes for Impure CO_2 Injection and Geochemical Impact on the Subsurface

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For the successful application of CCS technologies, it is critically important to understand the effects of impurities upon the performance of geological CO_2 storage operations. Various aspects of these processes are being studied by partners at UU and EWRE, including fluid/rock interactions, leakage of trace elements, and their impacts upon the subsurface environment. Laboratory and field-scale experiments are to be performed to assess the impact of impurities in the CO_2 stream on rock properties and its subsequent migration behaviour, and the overall effects upon the storage performance and caprock integrity. A significant component of the work will be a field-scale injection experiment at Heletz, Israel [12], where CO_2 will be co-injected with impurities and the effects analysed. Simultaneously, numerical models will be developed to understand the physical and chemical processes involving impure CO_2 more clearly, and in particular, the multiphase fluid phenomenon of CO_2 spreading/trapping and the acidic chemical environment induced by impurities.

Critical processes for impure CO_2 injection

There are many critical processes caused by subsurface CO_2 injection, which possibly exert negative impacts on the environment. CO_2 injection could lead to geochemical alteration and geomechanical deformation of the caprock, and alter its sealing capacity [13]. Co-injection with acidic species such as H_2S, SO_x and NO_x also enhances the solubility of many minerals including those containing significant concentrations of hazardous trace elements (e.g. As, Pb). In the event of release with CO_2, they are likely to exacerbate the impact upon groundwater quality by the formation of strong metal-sulfide complexes [14, 15]. Also supercritical CO_2 is itself an excellent solvent for toxic organic compounds such as benzene, which can potentially be mobilized through the occurrence of a leak [29].

Geochemical impact of impurities

In a Carbon Capture and Storage (CCS) scenario, CO_2 is injected for storage in a deep brine geological formation. Depending upon the CO_2 capture process, the injected CO_2 may contain various compositions of residual O_2, SO_x, NO_x, and inert gases. It is of interest to determine the environmental impact resulting from the inclusion of SO_2 in the CO_2 stream, and given the environmental and human health benefits of

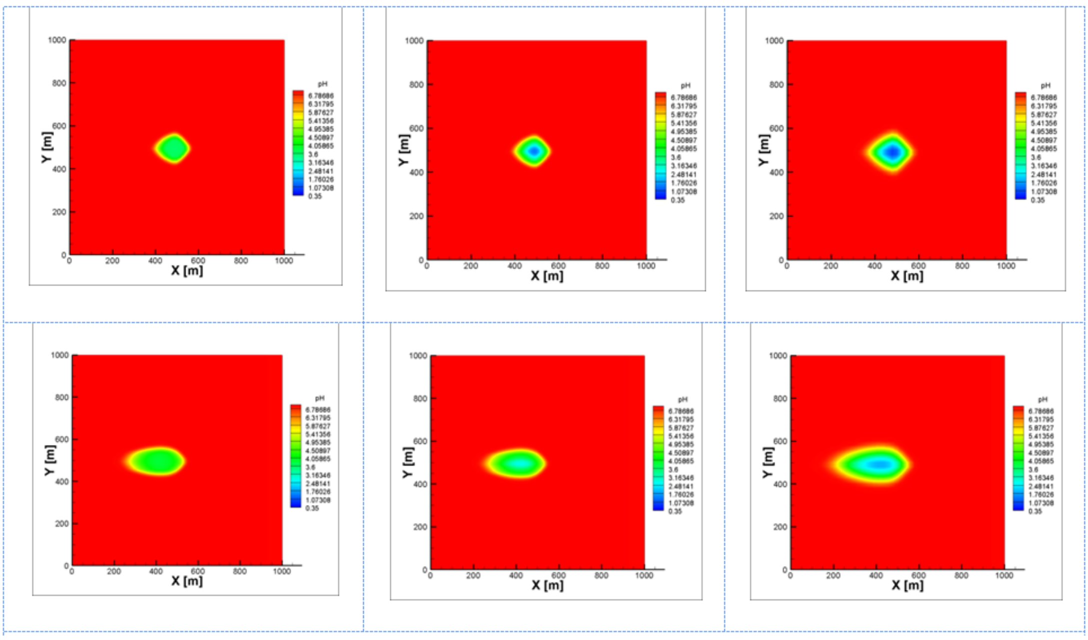

Figure 2. Predicted pH levels for pure CO_2 (left), 2% SO_2 (middle) and 4% SO_2 (right) after 1 year (top) and after 10 years (bottom) at a height of 20 meters from the bedrock.

controlling SO_2 emissions [16], it may be economically advantageous to dispose of SO_2 together with the CO_2.

The impact of the injection of CO_2 with an impurity level of 2% and 4% SO_2-CO_2 has been investigated. In the case of injection period of one week, the influence on the pH level is noticeable adjacent to the injection well, but its impact is insignificant near the reservoir ceiling. In the case of long term injection of pure and impure CO_2 streams, a significant impact upon the pH level is observed. Figure 2 shows the pH level at the ceiling of the reservoir, where the ceiling height is 20 m above the base. This model estimates the highest impact obtained by the presence of a significant amount of SO_2 in the injection stream. The model is developed using the PHREEQC software to evaluate the sulfate ion distribution, and also the PFLOTRAN code to predict the fate of the injection streams of SO_2-CO_2 and SO_2(aq) to the target storage reservoir. In addition, since corrosive water, having a low pH level, can induce changes in the physical properties of the caprock, this model can serve as the basis for investigations of the effect of SO_2 impurity on the impervious cap.

CO_2 Pipeline Rupture Experiments

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During the CO2PipeHaz project, a 256 m long, 20 mm diameter, fully instrumented pipeline, which was equipped with synchronous data acquisition devices was constructed on site in the Liaohe Oil field in China (Figure 3). This rig was used to obtain detailed data of experiments representing accidental puncture and full-bore releases using pure CO_2 as the working fluid. These data were subsequently used in the validation of the CFD models developed during the project, and provided insight into the dispersion behaviour of the escaping CO_2 following pipline rupture. In the CO2QUEST project this pipeline will be used to to conduct more complex release experiments involving the elucidation of ductile and brittle pipeline rupture phenomena. Hence, in addition to assisting the near-field modelling, data will be obtained for the validation of the fracture models.

Figure 3. The pipeline previously constructed in the Liaohe Oil Field (CO2PipeHaz project, August 2012).

It was discovered during the CO2PipeHaz project that the location of the pipeline in the oil field has a periodic risk of flooding, which previously caused delay to the experimental programme in CO2PipeHaz project, and could affect experiments in CO2QUEST. Therefore, in the CO2QUEST kick-off meeting it was decided to relocate the pipeline to a different test site. A suitable site was chosen to be Anbo in Dalian, which allows performance of the industrial-scale CO_2 release tests and is conveniently located in 151 km away from DUT (Figure 4).

Figure 4. Re-location of the CO_2 pipeline for the CO2QUEST project

The dismantling of the pipeline in Liaohe Oil Field was begun in March 2013, and in almost 5 months the pipeline was transported to the new test site. At the same time, the test site at Anbo was prepared for installation of the pipeline. Figure 5 shows the concrete pipeline support blocks constructed during the summer of 2013.

Figure 5. The concrete pipeline support blocks in the Anbo test site (summer 2013).

Figure 6. The pipeline re-assembled in the Anbo test site (September 2013).

Figure 6 shows a photo of the pipeline reassembled on the concrete blocks in the Anbo site. Following the pipeline re-assembly, it underwent successful water pressure test in October 2013.

The work presently in progress includes the design of the system for feeding impurities into the pipeline, and the instrumentation of the pipeline with transducers for the monitoring of pressure and temperature of CO_2 in the release experiments. This is in addition to the testing and the calibration of the equipment.

Techno-economic Assessment

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Whole-systems modelling

Partners at Imperial College London are applying a multi-scale modelling approach to the analysis of a CO_2 capture and transport system. Focus is upon the development of a series of scale-specific models which interact across a range of length and time scales. This approach is particularly relevant to the CO2QUEST project as the hour-to-hour behaviour of the CO_2 sources within a given decarbonised bubble will dictate the flow-rate and composition of the CO_2 in the transport network. This modelling approach is illustrated in Figure 7.

To date, in this work package, ICL have developed physically rigorous models of sub-critical, pulverised-coal fired power stations integrated with an amine-based post-combustion CO_2 capture process. Importantly, these models can describe both the design and off-design point operation of these systems. The captured CO_2 is then compressed and supplied to an associated transport network model. It is however, quite unlikely that a single source-to-sink network will be the final picture. Therefore, ICL have proposed a system-type model based on the three existing power stations in the UK: Drax, Didcot and Ratcliffe. We assume that the CO_2 from each of these sources is captured and hubbed at Skegness, and this model network is illustrated in Figure 8.

Then, using this model, we compare the ability of this model to reproduce the dynamic behaviour of the actual power plants. As can be observed from Figure 9, our proposed network model provides a reliable description of this system. However, a weakness of the current system model is that it only considers one power-capture pairing, i.e., coal and amines. Therefore, future work in this area must also consider gas-fired power plants and oxy-combustion technology. In particular, the design and operation of the oxy-combustion technology are important to this project. This is expanded upon in the following section.

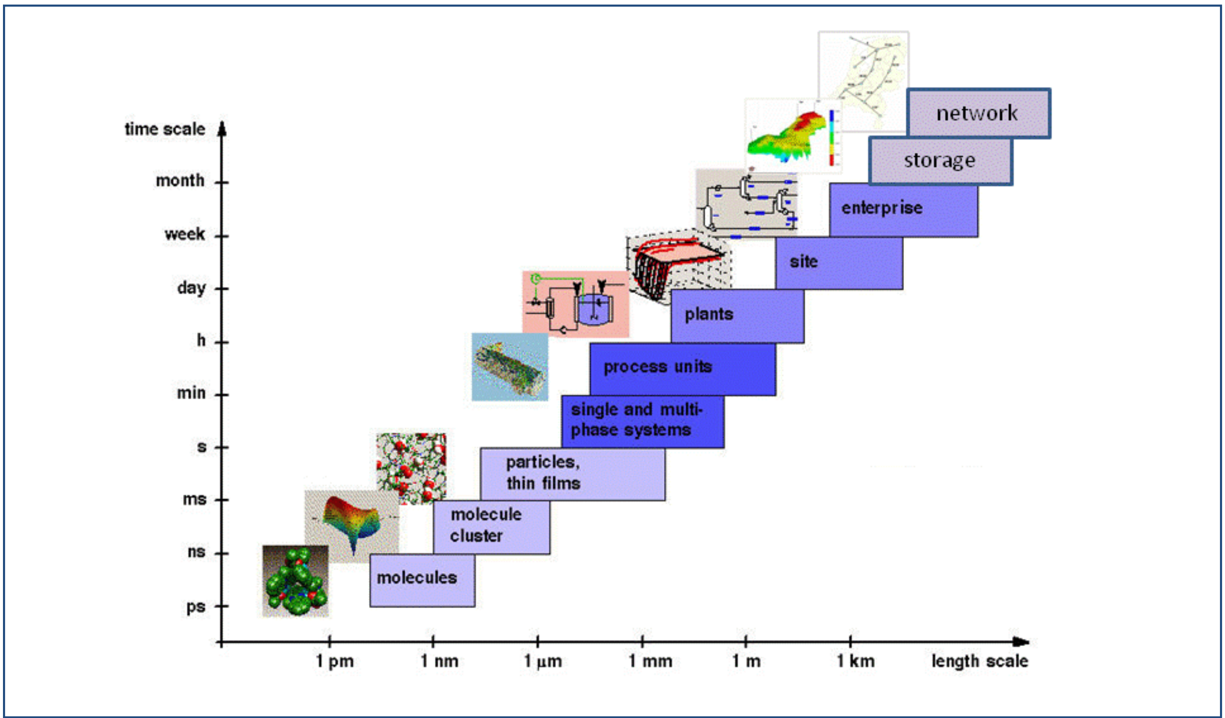

Figure 7. Multi-scale modelling approach

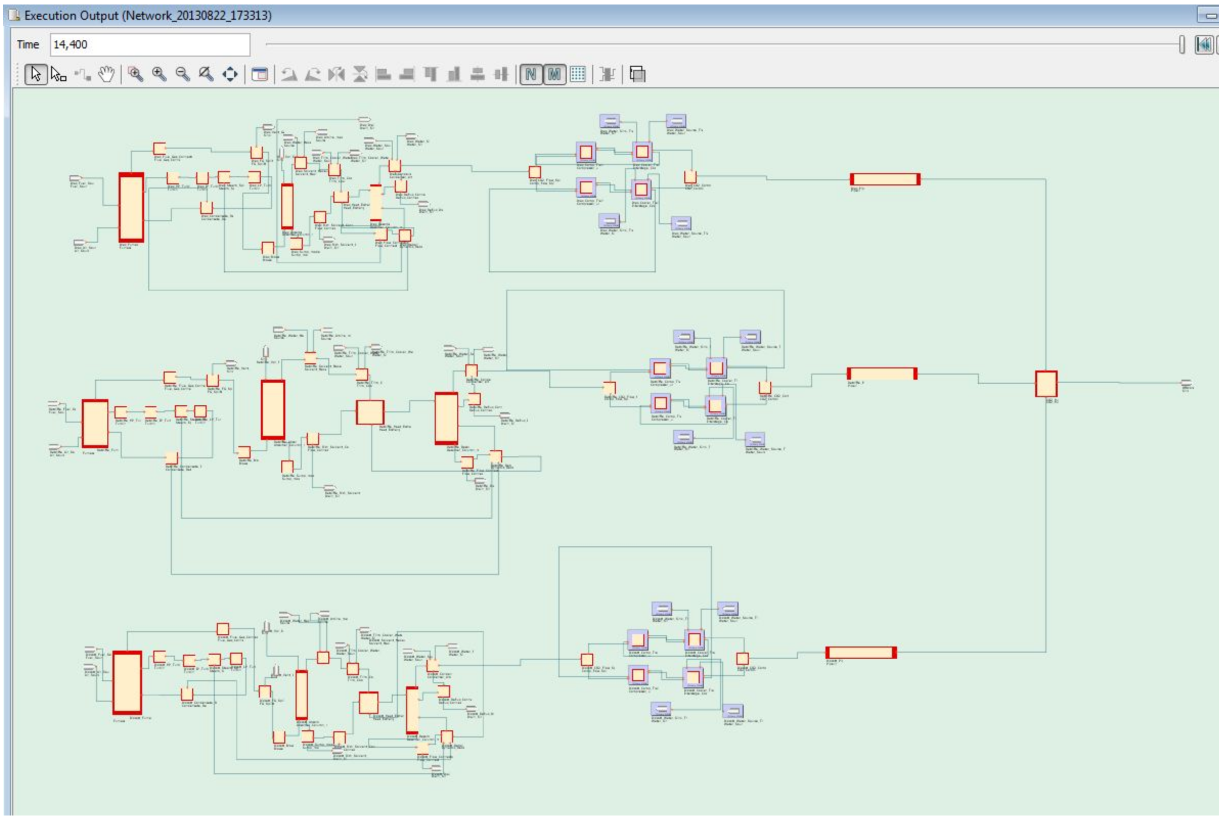

Figure 8. Proposed coal-fired and amine capture network.

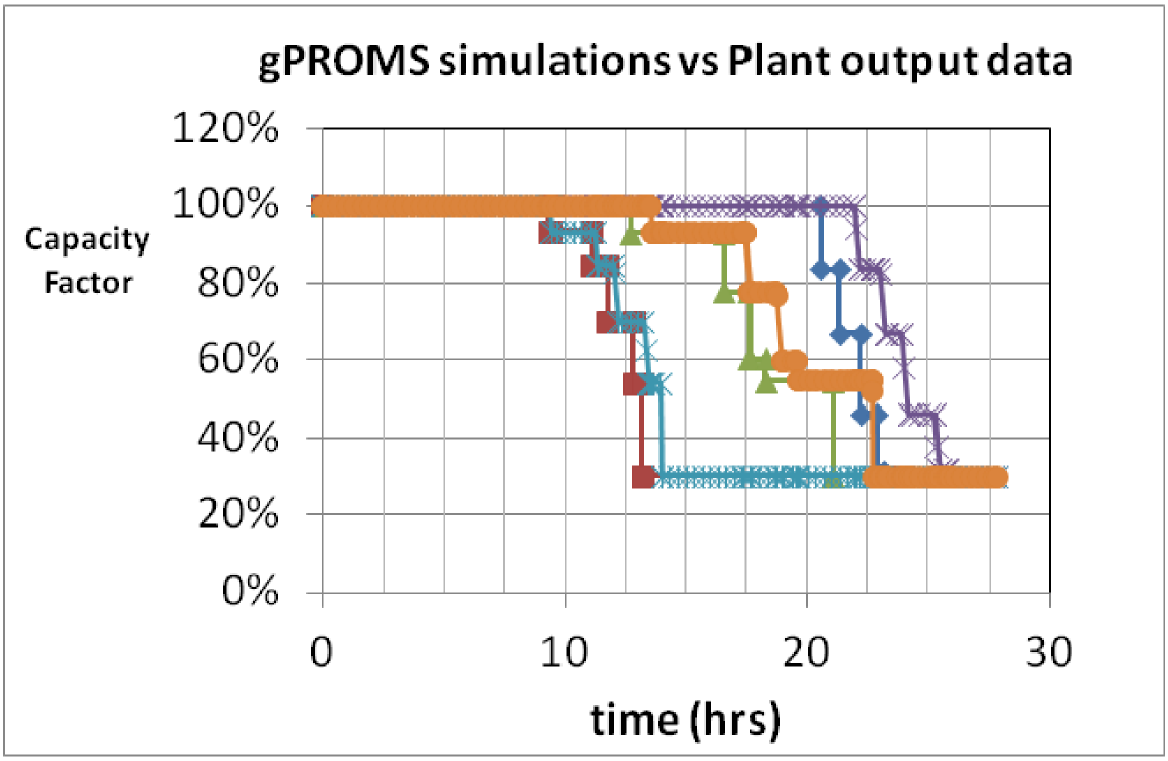

Figure 9. Comparison of gPROMS simulation with plant dispatch data.

Cost/Benefit Analysis

Given the number of potential sources for CO_2, both from the power and non-power sectors, it will be necessary to consider its source and also the capture technology with which it will be matched. Here there are three main options for the decarbonisation of electricity generation; pre-combustion, post-combustion and oxy-combustion. Whilst both pre-combustion and post-combustion technologies typically produce a CO_2 stream which is in excess of 98% pure, oxy-combustion technologies can produce a CO_2 stream where the composition varies in the range of 74 vol% < yCO2 < 99 vol%. This is illustrated in Table 1 [17] below.

	Typical composition of CO_2 stream arising from oxy-fuel combustion of pulverised coal		
	Raw / dehumidified	Double flashing	Distillation
CO_2 vol%	74.86	96.79	99.30
O_2 vol%	6.00	1.20	0.40
N_2 vol%	16.60	1.60	0.20
Ar vol%	2.30	0.40	0.10
NO_X vol%	0.071	0.015	
SO_2 vol%	0.070		
H_2O vol%	0.100		

Table 1. Typical composition of CO_2 stream arising from oxy-fuel combustion of pulverised coal**.**

Importantly, there are large differences in the specific cost of pure (>99%) CO_2 and raw (<80%) CO_2. Therefore, an important aspect of proposed future work will be the evaluation of the optimal configuration of the air separation unit.

Materials Selection and Fracture Models for Safe and Efficient Transport of CO_2

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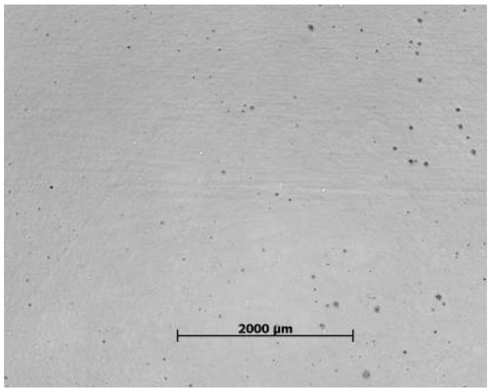
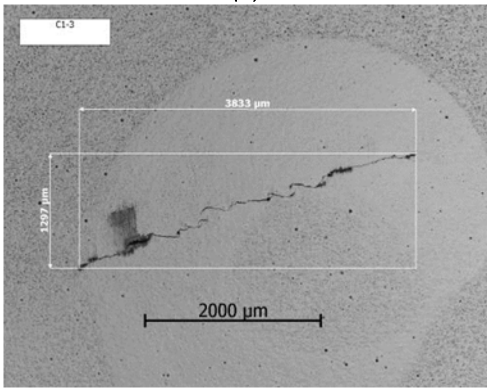
Determining the optimal steel grades/properties for efficient and safe transportation of CO_2 is a challenging task, especially when the CO_2 stream to be transported contains several different types of impurity elements such as SO_x, NO_x, moisture, and H_2S, etc. In case of leak/rupture of the pipelines, the decompression behaviour can substantially vary depending on the concentrations of the impurity elements mentioned above. Several challenges exist which are directly related to the material's properties such as (1) the local temperature drop during decompression in the pipeline which, if below the ductile to brittle transition temperature, can lead to extremely fast brittle fracture, (2) ductile running fracture would take place if the temperature is not low enough, but the material's resistance to crack propagation depends on the toughness of the steel, (3) possibility of sour corrosion cracking (see Figure 10) such as Hydrogen Induced Cracking (HIC) and Sulphide Stress Cracking (SSC) in the presence of H_2S.

To identify the required toughness of the pipeline steel material to resist the crack propagation or to arrest the crack rather quickly, first a computational fluid dynamics model will be developed by the UCL (University College London) team which will be used as an input (local temperature and pressure) of the fracture model. The type of fracture model (ductile or brittle) will depend on whether the temperature during decompression falls below the ductile to brittle transition temperature. Detailed experimental protocol has been designed which would allow to (1) determine the transition temperature of the pipeline steel materials



(a)



(b)

Figure 10. Examples showing (a) material resistant to sour corrosion cracking and (b) vulnerable to such cracking (sour grade implies materials resistant to HIC and SSC)

(Charpy and Battelle Drop Weight Tear tests), and (2) obtain the parameters needed to develop the fracture model such as force-displacement curves, J-R curve, CTOD, etc. In case of ductile fracture, modified Bai-Wierzbicki model will be used which can take into account the stress triaxiality, Lode angle, temperature effect, and strain rate, while for brittle fracture possible candidates are modified Ritchie-Knott-Rice (RKR), Beremin models, etc. As for the materials, three different materials grade have been chosen namely X65, X70, and X80. The first two grades are already used in the existing CO_2 pipelines, while the third grade (X80) is not yet in service but investigating this material may provide some insights on its possible use in the future for CO_2 transportation. Both sour and non-sour grades will be used for testing; in particular X65MS and X70MS materials (thermo-mechanically processed for sour service application) have been already obtained for the planned testing.

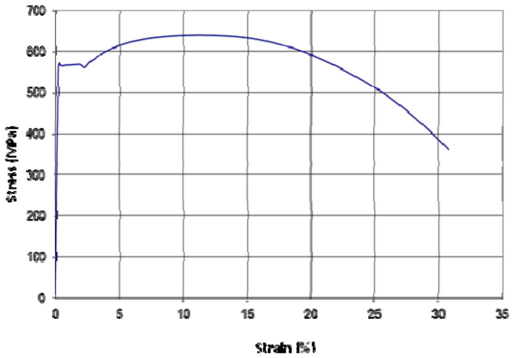


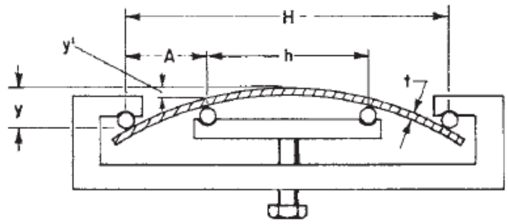
Figure 11. Stress Strain curve of X70MS material

Tensile tests have been conducted on the X70MS-14mm materials (see e.g. the tensile curve for X70MS material in Figure 11) and the results showed that the material meets the standard requirements for this grade such as yield and tensile strengths, yield/tensile ratio, elongation, etc. Sour service tests (HIC and SSC) were also performed according to NACE TM0284-2011 and NACE TM0177-2005/API 5L/EFC-16 standards and satisfactory results were obtained to qualify this steel as sour grade (see, e.g. Table 2 and Figure 12 for the SSC-FPB test results). Other tests such as notched tensile, single edge notch tensile (SENT), single edge notch bend (SENB), Charpy impact test, and Battelle Drop Weight Tear tests are currently being scheduled. A dynamic tear testing machine is planned to be upgraded in 2014 which will enable testing plates with large dimensions and full-wall thickness.

Table 2 SSC-FPB test results for the X70MS material (AYS = Actual Yield Strength)

Materials	Test Load	SSC Results
X70MS-14mm	90% AYS	No SSC cracks

In addition to the experimental testing, a modified Bai-Wierzbicki model is being developed for ductile fracture simulation which, as mentioned earlier, can take into account several important aspects of crack propagation, especially the stress triaxiality (η) and Lode angle (θ) (see Equation 1). The first version of the model has been already developed and it has been found that the yield locus is intermediate between Tresca and Von Mises. Simulations of the Battelle Drop Weight Tear tests are being carried out.



$$\sigma = \frac{12Ety}{3H^2 - 4A^2}$$

Figure 12. Schematic of Sulphide Stress Cracking (SSC) test - Four Point Bending (σ is the desired stress level, E is the elastic modulus)

For brittle fracture, some possible models are being evaluated such as the modified RKR model. According to RKR model which "cleavage fracture" occurs if $\sigma_{yy} > \sigma f$ over a characteristic distance where, σ_{yy} = maximum principal stress, and σf = critical stress. For Modified RKR, the conditions are as follows: $\epsilon_p \geq \epsilon_{pc}$, $\sigma_m/\sigma_e \geq Tc$, $\sigma_{yy} \geq \sigma_f$ where, σ_m = hydrostatic stress, σ_e = equivalent stress, and Tc = critical stress triaxiality.

Next steps

The first round of mechanical characterization of the materials (X65, X70, and X80) such as smooth tensile and notched tensile as well as the Charpy impact testing and Battelle Drop Weight Tear testing are expected to be completed by February 2014, while the target completion date for some

$$\sigma_{yld} = \bar{\sigma}(\varepsilon_p)\cdot\underbrace{\left[\varepsilon^m + \delta\varepsilon\right]}_{\text{Strain Rate}}\cdot\overbrace{\left[\frac{\alpha}{T^\beta}\right]}^{\text{Temperature}}\cdot\underbrace{\left[1 - c_\eta\cdot(\eta - \eta_0)\right]}_{\text{Stress Triaxiality}}\cdot\overbrace{\left[c_\theta^s + \left(c_\theta^{ax} - c_\theta^s\right)\cdot\left(\gamma - \frac{\gamma^{m+1}}{m+1}\right)\right]}^{\text{Lode Angle}}$$

Equation 1. Modified Bai-Wierzbicki model.

other tests such as plain strain tensile tests, SENT, SENB, and dynamic tear testing is September 2014. Both the ductile and brittle fracture model developments will continue simultaneously.

Modelling Solid-Fluid Equilibria using the Yokozeki EoS

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Accurate modelling of solid-fluid equilibria of pure CO_2 is essential when simulating CO_2 pipeline depressurization that reaches conditions below the CO_2 triple point. In this work, a new Equation of State, which extends below the triple point, is considered. The model is a modification of the original model proposed by Yokozeki [18]. It expresses the pressure as a 'high order' equation with respect to temperature and density as follows:

$$P = \frac{RT}{V-b}\left(\frac{V-d}{V-c}\right) - \frac{a}{V^2}$$

The model can predict pure CO_2 properties over the entire phase diagram including solid, vapour and liquid regions. The Yokozeki approach is semi-empirical in nature but thermodynamically consistent. It attracts increased interest by the engineering community because of its ability to model the entire phase diagram with a relatively simple mathematical form.

The new Equation of State has two significant differences when compared to classical Cubic Equations of State. Firstly, it introduces a discontinuity in the pressure-density relation of the repulsive part of the Van der Waals term. It is not clear if this discontinuity is necessary for predicting the solid-fluid equilibrium or if a discontinuity in the compressibility is sufficient to describe solid-fluid phase transitions. Secondly, in contrast to the cubic Equation of State, the parameters are not uniquely determined as a function of the critical temperature and the pressure. Cubic EoS have parameters uniquely defined by the values of the critical Temperature T_c and pressure P_c and, as result, the critical compressibility factor $Z_c = P_cV_c/(RT_c)$ has the same value for all substances described by the same EoS. In the Yokozeki EoS, the existence of two additional parameters results in two additional degrees of freedom which have to be specified.

Thus, the Yokozeki model parameters can be found as a function of T_c and P_c and two additional variables (i.e Z_c and *b)*. In order to get a quantitative representation, Yokozeki proposed two parameters; the so-called temperature dependence of the strength of interactions and the excluded volume parameter b.

In order to calculate the phase equilibria between the solid and the vapour phase, the chemical potential of each phase must be equated. This condition graphically corresponds to an 'equal area' condition in the Pressure-Volume diagram as shown in Figure 13. This is similar to the case of vapour-liquid equilibria with the difference being that the integration must be performed around a singularity point.

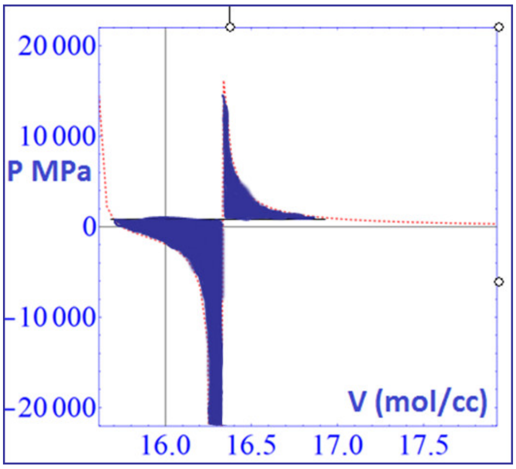

Figure 13. Equal area dictates the equilibration of the chemical potential between vapour and solid phases in the Yokozeki EoS

The Yokozeki model is being evaluated against available experimental data and other models available for predicting solid-vapour equilibria for pure CO_2 [19]. Preliminary results show that the model can accurately predict equilibria properties such as sublimation pressure (Figure 14), densities (Figure 15) and enthalpies (Figure 16). Overall good agreement is obtained except for the enthalpy of sublimation which will be explored further. An extension to mixtures will also be considered in our attempt to model the effect of impurities on the conditions that lead to dry-ice formation.

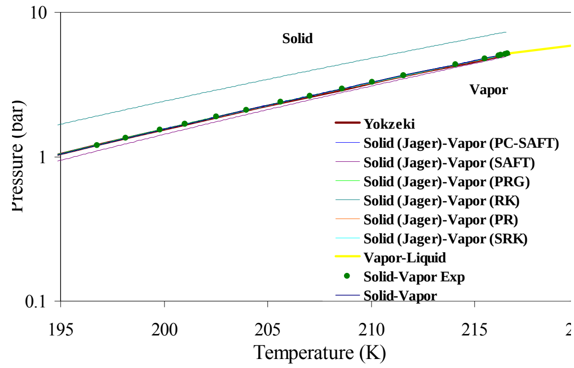

Figure 14. Comparison between model predictions and experimental data for the sublimation pressure of pure CO_2. Models are based on Yokozeki Model and other models which use a variety of EoS to account for the vapour phase and the free energy EoS introduced by Jager and Span [20] to account for the solid phase.

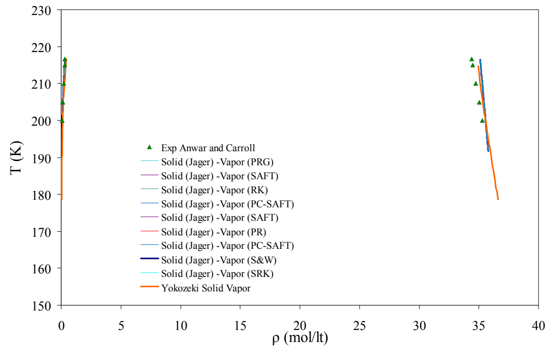

Figure 15. Comparison between model predictions and experimental data for the vapor and solid density at sublimation for pure CO_2. Models are based on Yokozeki Model and other models which use a variety of EoS to account for the vapor phase and the free energy EoS introduced by Jager and Span to account for the solid phase.

Review of available experimental data for CO_2 and CO_2 mixtures with impurities of interest to CCS. Experimental Gaps.

An extensive literature review for experimental data regarding properties of CO_2 mixtures was carried out during this period. The review included VLE, volumetric and derivative thermodynamic properties and transport properties. A database indexed by system and property was build in order to assess experimental gaps and validate thermodynamic models of interest to CCS.

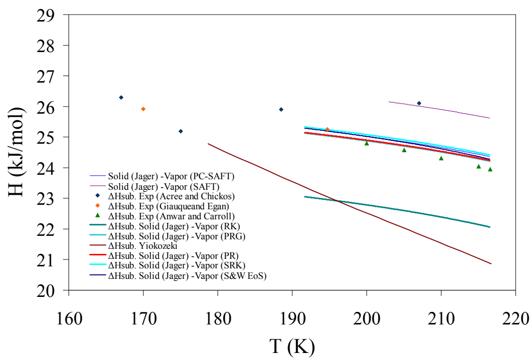

Figure 16. Comparison between model predictions and experimental data for the enthalpy of sublimation of pure CO_2. Models are based on Yokozeki Model and other models which use a variety of EoS to account for the vapour phase and the free energy EoS introduced by Jager and Span to account for the solid phase.

Knowledge gaps were identified for the majority of CO_2 mixtures with impurities and properties of interest to CCS technology. More specifically, the literature review showed that the only property in abundance in the literature was the vapour-liquid equilibria pressure of saturation of binary mixtures (Figure 17). Derivative properties and transport properties were also searched for in the literature, giving a small number of data. As the complexity of the mixtures increases in terms of number of components and conditions, the data become scarcer. In fact, the experimental data for isothermal compressibility found for the system CO_2-N_2-CH_4-H_2 [21], as well as the phase envelope, density, and viscosity for the system CO_2-N_2-O_2-Ar [22], are the most complex cases of CO_2 mixtures with gases that exist in the literature.

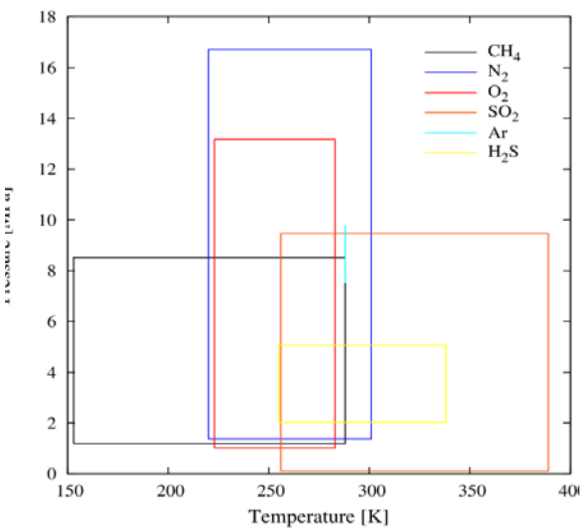

Figure 17. Range of conditions of data for binary VLE data.

Based on these findings, and the needs for validating the newly developed thermodynamic models, a matrix of VLE experiments have been indentified and proposed to project partners. A more in-depth analysis of the available data, as well as the suggestions for further experimental investigations can be found in the project deliverable 1.7 report.

Development of Near-field Dispersion Model

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The objectives of the near-field dispersion Work Package includes the development of a computational fluid dynamic (CFD) model capable of predicting the near-field structure of high pressure releases of supercritical, dense phase and gaseous CO_2 containing impurities typical of those to be encountered in an integrated CCS chain, including an equation of state that covers CO_2 with impurities (NCSR) and models for the formation of liquid droplets and solid particles. Integral to this development is the validation of the CFD model derived against experimental data available in the literature, and to be generated as part of the project by partners at INERIS and DUT. The usefulness of this CFD model will also be demonstrated (UoL and INERIS) by interfacing its predictions for a number of realistic release scenarios, with existing far-field dispersion models, in order to predict hazards at large distances for use in risk assessments.

The fundamentals of this fluid dynamic model have been discussed in the literature [23, 24], which forms a basis for the development of the multi-component model to describe CO_2 with impurities. Briefly, the code obtains solutions of the time-dependent, Favre-averaged (density-weighted) forms of the transport equations for mass, momentum, and total energy (internal energy plus kinetic energy). Integration of the equations employs a second-order accurate, upwind, finite-volume scheme in which the transport equations are discretised following a conservative control-volume approach, with values of the dependent variables being stored at the computational cell centres. Approximation of the diffusion and source terms is undertaken using central differencing, and an HLL [25], second-order accurate variant of Godunov's method is applied with respect to the convective and pressure fluxes.

The calculations also employed an adaptive finite-volume grid algorithm which uses a three-dimensional rectangular mesh with grid adaption achieved by the successive overlaying of refined layers of computational mesh. Figure 18 demonstrates this technique in a two-dimensional planar calculation of the near-field of a sonic CO_2 release. Where there are steep gradients of variable magnitudes such as at flow boundaries or discontinuities such as the Mach disc, the mesh is more refined than in areas such as the free stream of the surrounding fluid.

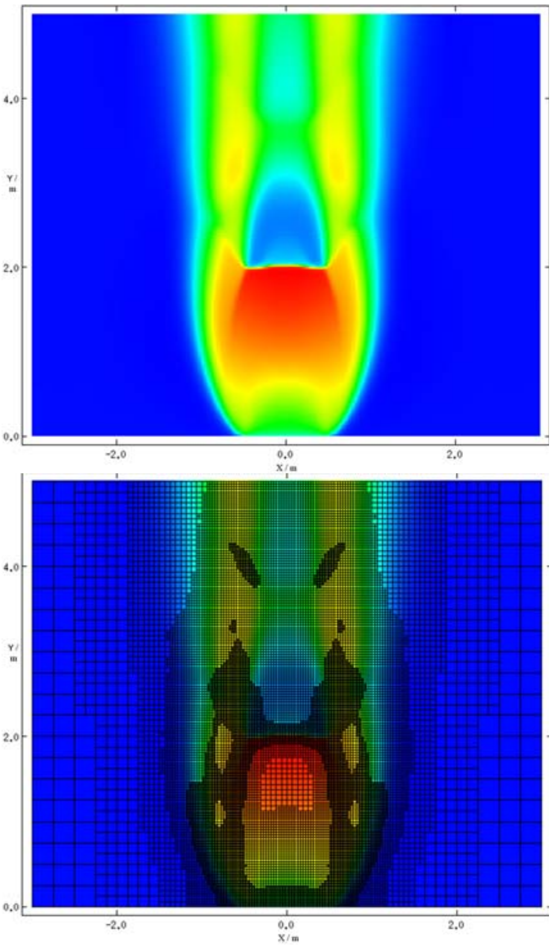

Figure 18. Adaptive mesh refinement grid mapped onto mean velocity predictions in the region of a Mach disc.

Representation of the Reynolds stresses, and hence the closure of the equation set, was initially achieved via the k-ε turbulence model [26] using a compressibility correction attributed to Sarkar et al. [27]. Figure 15 demonstrates the effectiveness of the compressibility correction as applied in the modelling of an under-expanded air jet. The most recent development in this area of turbulence modelling is the inclusion of a second-moment transport model for the Reynolds stresses into the code. As can be seen in a comparison of Figures 19 and 20, the unmodified second-moment model notably out-

performs the modified two-equation model when applied to the air-jet case.

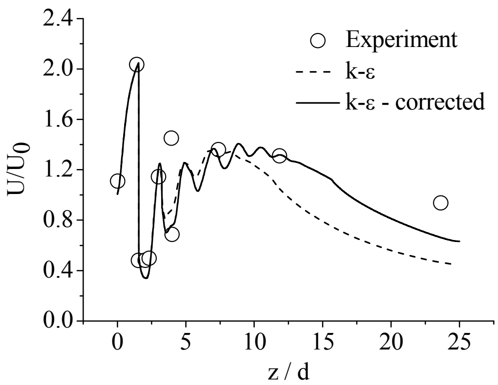

Figure 19. Predictions of an under-expanded air jet using both a corrected and uncorrected k-ε model.

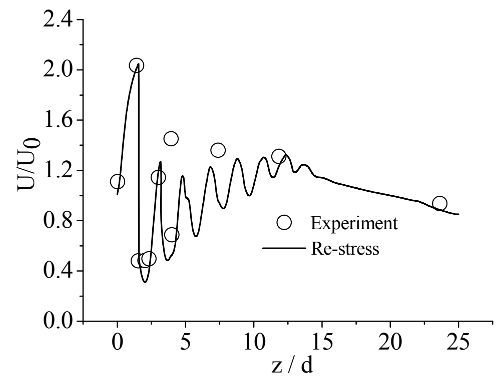

Figure 20. Predictions of an under-expanded air jet using an un-modified second-moment turbulence model.

Work being undertaken at the moment includes the development of compressible closures for terms in the Reynolds-stress transport equations not explicitly defined in their derivation.

An essential prerequisite for computational studies of the behaviour of materials is to have an accurate formulation for the description of their thermodynamic properties, applicable over a wide range of pressures and temperatures. Due to the well-known shortcomings of the Peng-Robinson [28] and Span and Wagner [29] equations of state for carbon dioxide, a composite equation of state has been constructed for pure CO_2 systems which accounts for all three phases present in the releases under investigation. The gas phase is computed from Peng-Robinson, the liquid phase from Span and Wagner, and the latent heat of fusion and solid phase from the DIPPR tables given in the Knovel library [30]. Additionally, vapour pressures below the triple point are tabulated from Span and Wagner. Figure 21 shows the phase envelopes of internal energy predicted by this composite methodology, and the importance of the consideration of the latent heat of fusion is clearly observable. Work now being undertaken in conjunction with partners NCSRD will extend these capabilities to account for the thermodynamic behaviour of impure CO_2 systems.

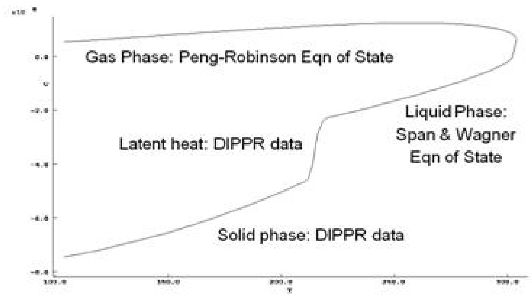

Figure 21. Predictions of pure CO_2 internal energy plotted against temperature using the novel composite equation of state.

Further development of the UoL model will be undertaken to incorporate the accurate three-dimensional, time-dependent modelling of transmission pipe-wall and crack-tip interactions with the flow. It has been shown that changes in pipeline temperature by as little as 10 degrees can result in the transformation of a short crack into a fast-running long fracture [31]. It is expected that Joule-Thomson cooling will be notably affected by the presence of impurities in an accidental release, and hence detailed transient three-dimensional temperature and pressure profile predictions in the location of any pipeline puncture or rupture will be required to provide input to the crack propagation modelling proposed by partners at UCL and OCAS.

Therefore, the UoL model will be further extended to accurately model conjugate heat transfer with respect to the pipe/vapour, pipe/liquid, solid/liquid, and vapour/liquid interfaces. Additionally, realistic release scenarios will be investigated in terms of the modelling of non-spherical release holes, and crack tips.

Shallow Water Aquifer Injection Tests at Catenoy

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To contribute to the work investigating the effects of CO_2 quality on storage behaviour, INERIS will be conducting a monitored injection experiment at the Catenoy site in France.

The long-term impacts of injecting anthropogenic CO_2 into subsurface storage volumes is currently not well known. Factors such as the rate of injection, migration of CO_2 after injection, the interaction of the CO_2 with the surrounding environment, and the risk of CO_2 leakage are all factors that are expected to be influenced by the composition of the CO_2 being injected. Issues of CO_2 migration and leakage are of special importance, especially for land based reservoirs, where leakage could pose problems for agriculture or the public.

To investigate the consequences of injecting CO_2 into subsurface aquifers, INERIS will prepare and instrument an injection well into an aquifer 25 m below ground level in Catenoy. The site will be instrumented to monitor subterranean conditions up to 10 m upstream and 50 m downstream of the injection point (Figure 22). Within these distances, the measurements will be taken at various depths to monitor water quality, and the concentration of gases immediately above the aquifer and just below ground level.

Assuming that CO_2 is derived from an industrial source, such as a fossil fuel power station, impurities such as N_2, O_2, Ar and H_2O can be added to the CO_2 before injection. Additional impurities such as H_2S, SO_x and NO_x and appropriate trace elements and organic compounds may be added subject to approval from the relevant administrative bodies. The possibility of injecting CO_2 mixture captured from a fossil fuel power station using the test facilities available to one of the project partners is also being investigated.

It is proposed to begin the injection from early 2015. The researchers will monitor the site throughout injection and for a period of time after injection is completed.

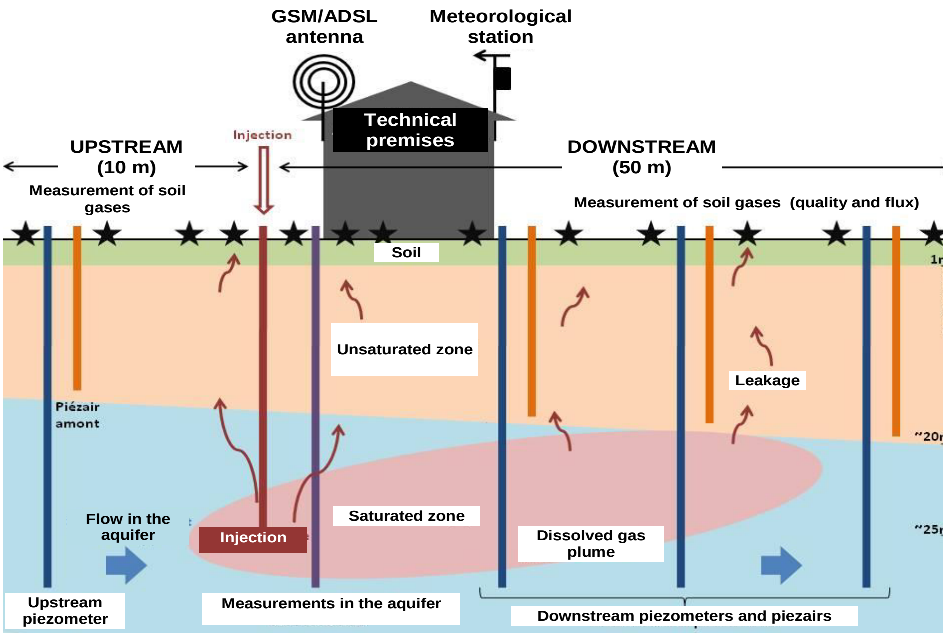

Figure 22. Schematic illustration of injection of CO_2 mixture into a shallow aquifer at Catenoy and associated monitoring equipment

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