Process Safety and Environmental Protection

rok 2014, ročník 92

Číslo 1 (January 2014)

Henk W.M. Witlox, Mike Harper, Adeyemi Oke, Jan Stene. *Validation of discharge and atmospheric dispersion for unpressurised and pressurised carbon dioxide releases.* Pages 3–16.

This paper discusses the validation of discharge and subsequent atmospheric dispersion for both unpressurised and pressurised carbon dioxide releases using the consequence modelling package Phast.

The paper first summarises the validation of the Phast dispersion model (UDM) for unpressurised releases. This includes heavy gas dispersion from either a ground-level line source (McQuaid wind-tunnel experiments) or an area source (Kit-Fox field experiments). For the McQuaid experiments minor modifications of the UDM were made to support line sources. For the Kit Fox experiments steady-state and 20-s finite-duration releases were simulated for both neutral and stable conditions. Most accurate predictions of the concentrations for finite duration releases were obtained using the UDM Finite Duration Correction method.

Using experiments funded by BP and Shell and made available via DNV's CO2PIPETRANS JIP, the paper secondly summarises the validation of the Phast discharge and dispersion models for pressurised CO_2releases. This modelling accounted for the possible presence of the solid CO_2 phase following expansion to atmospheric pressure. These experiments included both high-pressure steady-state and time-varying cold releases (liquid storage) and high-pressure time-varying supercritical hot releases. Both the flow rate and the concentrations were found to be predicted accurately.

The above validation was carried out with no fitting whatsoever of the Phast extended discharge and dispersion models.

- **Keywords:** CO_2; Consequence modelling; Model validation; Discharge; Atmospheric dispersion; Thermodynamics

Alison McGillivray, Ju Lynne Saw, Diego Lisbona, Mike Wardman, Mike Bilio. *A risk assessment methodology for high pressure CO_2 pipelines using integral consequence modelling.* Pages 17–26.

This paper presents a risk assessment methodology for high pressure CO_2 pipelines developed at the Health and Safety Laboratory (HSL) as part of the EU FP7 CO2Pipehaz project. Until recently, risk assessment of dense phase and supercritical CO_2 pipelines has been problematic because of the lack of suitable source term and integral

consequence models that handle the complex behaviour of CO_2 appropriately. The risk assessment presented uses Phast, a commercially available source term and dispersion model that has been recently updated to handle the effects of solid CO_2. A test case pipeline was input to Phast and dispersion footprints to different levels of harm (dangerous toxic load and probit values) were obtained for a set of pipeline specific scenarios. HSL's risk assessment tool QuickRisk was then used to calculate the individual and societal risk surrounding the pipeline. Knowledge gaps that were encountered such as: harm criteria, failure rates and release scenarios were identified and are discussed.

- **Keywords:** CCS; Carbon dioxide; Pipelines; Phast; Risk assessment; CO2Pipehaz

Diego Lisbona, Alison McGillivray, Ju Lynne Saw, Simon Gant, Mike Bilio, Mike Wardman. ***Risk assessment methodology for high-pressure CO_2 pipelines incorporating topography.*** **Pages 27–35.**

This paper presents a risk assessment methodology for high-pressure CO_2 pipelines developed at the Health and Safety Laboratory as part of the EU FP7 project CO2Pipehaz.

Traditionally, consequence modelling of dense gas releases from pipelines at major hazard impact levels is performed using integral models with limited or no consideration being given to weather bias or topographical features of the surrounding terrain. Whilst dispersion modelling of CO_2 releases from pipelines using three-dimensional CFD models may provide higher levels of confidence in the predicted behaviour of the cloud, the use of such models is resource-intensive and usually impracticable. An alternative is to use more computationally efficient shallow layer or Lagrangian dispersion models that are able to account for the effects of topography whilst generating results within a reasonably short time frame.

In the present work, the proposed risk assessment methodology for CO_2 pipelines is demonstrated using a shallow-layer dispersion model to generate contours from a sequence of release points along the pipeline. The simulations use realistic terrain taken from UK topographical data. Individual and societal risk levels in the vicinity of the pipeline are calculated using the Health and Safety Laboratory's risk assessment tool QuickRisk.

Currently, the source term for a CO_2 release is not well understood because of its complex thermodynamic properties and its tendency to form solid particles under specific pressure and temperature conditions. This is a key knowledge gap and any subsequent dispersion modelling, particularly when including topography, may be affected by the accuracy of the source term.

- **Keywords:** CCS; CO_2; Pipelines; Shallow layer; Societal risk; QuickRisk

Sergey Martynov, Solomon Brown, Haroun Mahgerefteh, Vikram Sundara, Shaoyun Chen, Yongchun Zhang. ***Modelling three-phase releases of carbon dioxide from high-pressure pipelines.*** **Pages 36–46.**

This paper describes the development and experimental validation of a three-phase flow model for predicting the transient outflow following the failure of pressurised CO_2 pipelines and vessels. The choked flow parameters at the rupture plane, spanning the dense-phase and saturated conditions to below the triple point, are modelled by maximisation of the mass flowrate with respect to pressure and solids mass fraction at the triple point. The pertinent solid/vapour/liquid phase equilibrium data are predicted using an extended Peng–Robinson equation of state.

The proposed outflow model is successfully validated against experimental data obtained from high-pressure CO_2 releases performed as part of the FP7 CO2PipeHaz project (www.co2pipehaz.eu).

The formation of solid phase CO_2 at the triple point is marked by a stabilisation in pressure as confirmed by both theory and experimental observation. For a fixed diameter hypothetical pipeline at 100 bar and 20 °C, the flow model is used to determine the impact of the pipeline length on the time taken to commence solid CO_2 discharge following its rupture.

- **Keywords:** Pipeline transportation; Accidental discharge; CO_2; Choked flow; Triple point; Homogenous equilibrium model

Renato Benintendi. ***Non-equilibrium phenomena in carbon dioxide expansion***. **Pages 47–59.**

Release of liquid and supercritical carbon dioxide is a fundamental research topic in CCS. Traditional approach is largely based on HEM and, in general, assumes equilibrium from the outlet to the Mach disc. Experimental results have shown that this approach is not always effective in describing the expansion phenomenon; therefore a significant lack of knowledge exists about CO_2 properties at the under-expanded jet zone boundary, which is a main focus in process safety. Here, solid formation, vapour quality, sonic velocity and final temperature are generally calculated according to equilibrium saturation condition, and this is generally incorrect. This article deals with non-equilibrium thermodynamics of liquid and supercritical CO_2expansion, illustrating relaxation dynamics through the HRM models, and discussing the very specific singularities of CO_2 phase transitions, vapour to liquid and liquid to solid, that result away from the equilibrium condition, due to the rapid phase changes and to the specific properties of CO_2 multi phase thermodynamics, including nucleation and particle growth. Statistical rate theory has been applied with the aim at identifying the phase transition energy barrier, resulting in a significant entropy increase. A case study based on HEM conservation equations integrated with the statistical rate approach has been presented, which covers the gap of the equilibrium hypothesis. The objective of the article is to provide a more accurate method to predict the properties of carbon dioxide following an expansion.

- **Keywords:** CCS; Carbon dioxide; Non-equilibrium thermodynamics; HRM; Metastability; Statistic rate theory;Adiabatic expansion; QRA

Sang Heon Han, Daejun Chang, Jooil Kim, Wonhee Chang. ***Experimental investigation of the flow characteristics of jettisoning in a CO_2 carrier.*** **Pages 60–69.**

This experimental study was performed to investigate the flow characteristics in the jettisoning flow line of a liquid CO_2 carrier. When a pressurized liquid CO_2 container loses mechanical integrity, possibly by material or mechanical defects, the liquid inventory should be drained out rapidly for safety reasons using the so-called jettisoning process. In the course of jettisoning, the liquid CO_2 undergoes two phase change stages, from liquid to liquid + vapor and from liquid + vapor to solid + vapor. Consequently, the jettisoning release rate is affected by the characteristics of these phase changes. In this study, liquid CO_2 was discharged through a small tube, representing a jettisoning flow line. The temperature and pressure were measured along the tube, and the locations of the phase changes were inferred from the measured data. The experimental results showed that active nucleation occurred near the tube tip and that the phase change into solid and vapor occurred just after leaving the pipe, irrespective of the tube length in this study.

- **Keywords:** Jettisoning; CO_2 carrier; Liquid CO_2 release; Phase change; Jettisoning flow line; Nucleation

Giorgia De Guido, Stefano Langè, Stefania Moioli, Laura A. Pellegrini. *Thermodynamic method for the prediction of solid CO_2 formation from multicomponent mixtures.* Pages 70–79.

The increase in GHG concentration has a direct effect on global climate conditions. Among the possible technologies to mitigate GHG emissions, CCS is being accepted to gain emission reduction. Such technology also involves cryogenic CO_2 capture processes based on CO_2 freeze-out or where the formation of solid CO_2 must be avoided. Captured CO_2 is usually transported in pipelines for the reinjection.

The risk associated to the release of CO_2 is due to the changing temperatures and pressures the system may experience, which can lead to the deposition of solid CO_2 where it must be avoided. Prolonged exposure to dry ice can cause severe skin damage and its resublimation could pose a danger of hypercapnia. It is, thus, necessary to build up a tool able to predict the conditions in which CO_2 can freeze-out.

A thermodynamic methodology based on cubic EoSs has been developed which is able to predict solid–liquid–vapor equilibrium of CO_2 mixtures with *n*-alkanes or H_2S which are usually found in equipment for acidic gas, mainly natural gas, treatment.

The focus is a detailed analysis of the method performances when more than two components are present since, for such a case, literature does not provide significant modeling results.

- **Keywords:** Carbon dioxide; Hydrogen sulfide; Freeze-out; Solid–liquid–vapor equilibrium; SRK; PR

Qing Zhao, Yu-Xing Li. *The influence of impurities on the transportation safety of an anthropogenic CO_2 pipeline.* Pages 80–92.

Transportation safety is a key aspect of carbon capture and storage (CCS), which is a major technology used to reduce greenhouse gas emissions. Supercritical CO_2 pipelines have been certified as an optimised choice for CO_2 transportation. The results of this study show that the Peng–Robinson (PR) equation of state is recommended for analysis of the properties of supercritical CO_2. The influence of nonpolar and polar impurities on the two-phase region and the location of the sharp discontinuity in the density are found by analysing the ternary phase equilibrium and physical parameters using the PR equation of state. A transitional area between the supercritical phase and the dense phase, where the density changes abruptly, is defined as the quasi-critical region. This study describes the functional relation between the temperature and the pressure that defines the quasi-critical line by calculating the partial derivative equations and then determines the effect of impurities on the quasi-critical region of transported CO_2. Operational recommendations for pipeline transportation of flue CO_2 are developed using a pipeline operated by Sinopec as an example, demonstrating the influence of impurities in flue CO_2 on saturation pressure for control and prevention of fractures in CO_2 pipelines.

- **Keywords:** CCS; Carbon dioxide; Pipeline transportation; Impurity; Quasi-critical; Saturation pressure

Nicola Paltrinieri, Jill Wilday, Mike Wardman, Valerio Cozzani. *Surface installations intended for Carbon Capture and Sequestration: Atypical accident scenarios and their identification.* Pages 93–107.

With the advent of Carbon Capture and Sequestration (CCS) technology the extent of CO_2 handling is set to increase dramatically. However, lack of substantial operational experience in such a novel process can lead to significant difficulties in identifying the associated hazards. This field may be characterized by atypical accident scenarios, i.e. scenarios not captured by common HAZard IDentification (HAZID) techniques because of omissions, errors or lack of knowledge. Recent atypical events evidence that consequences may exceed by far those of worst-case reference scenarios. Identification of atypical scenarios related to CCS is a challenge, considering also the public concern that this technology raises. This study focuses on new and emerging technologies of carbon capture and transport. A HAZID analysis was carried out by means of two different approaches ('top-down' and 'DyPASI'). This allowed not only for a double check of results, but also for the comparative assessment of the methodologies and of their applicability. A general overview of the accident scenarios related to these technologies was given. No absolute showstoppers were found. Rather, a number of potential hazards were identified which will require the adoption of safe design principles to eliminate, prevent, control or mitigate them. Some possible safety barriers required for implementation were identified as a starting point in this process.

- **Keywords:** CCS; HAZID; Atypical scenarios; DyPASI; Top-down approach

O. Yevtushenko, D. Bettge, S. Bohraus, R. Bäßler, A. Pfennig, A. Kranzmann. *Corrosion behavior of steels for CO_2 injection.* Pages 108–118.

The process chain for Carbon Capture and Sequestration (CCS) includes tubing for injection of CO_2 into saline aquifers. The compressed CO_2 is likely to contain specific impurities; small concentrations of $SO_2$and NO_2 in combination with oxygen and humidity are most harmful. In addition, CO_2 saturated brine is supposed to rise in the well when the injection process is interrupted. The material selection has to ensure that neither CO_2 nor brine or a combination of both will leak out of the inner tubing. In this comprehensive paper the investigated materials range from low-alloy steels and 13% Cr steels up to high-alloy materials. Electrochemical tests as well as long term exposure tests were performed in CO_2, in brine and combination of both; pressure was up to 100 bar, temperature up to 60 °C. Whereas the CO_2 stream itself can be handled using low alloy steels, combinations of CO_2 and brine require more resistant materials to control the strong tendency to pitting corrosion. The corrosion behavior of heat-treated steels depends on factors such as microstructure and carbon content. For different sections of the injection tube, appropriate materials should be used to guarantee safety and consider cost effectiveness.

- **Keywords:** CCS; Injection tubing; Corrosion; Safety; Carbon steel; High alloy steel; Saline fluid; Supercritical CO_2

G. Gallastegui, A. Barona, N. Rojo, L. Gurtubay, A. Elías. *Comparative response of two organic biofilters treating ethylbenzene and toluene after prolonged exposure.* Pages 112–122.

The response of two biofilters filled with an organic waste material for treating ethylbenzene and toluene was studied for 415 and 472 operating days, respectively. The peak elimination capacities (EC_{MAX}) recorded were 170 g m^{-3} h^{-1} for ethylbenzene

(EC_{MAX}) and 138 g m^{-3} h^{-1} for toluene. Regarding the degradation profile through the biofilters, an increase in the inlet concentration displaced the degradation profile into the downstream section. A sudden decrease in the performance of both biofilters occurred when the moisture content (MC) of the packing material exceeded 37% for ethylbenzene and 30% for toluene. Thus, a recommended MC value was established in the 15–30% range. Given the bioreactor was operated at a low MC level, fungi prevailed over bacteria. Nevertheless, synergism was detected between both microorganism types for the mineralization of the aromatic hydrocarbons.

- **Keywords:** Biofiltration; Toluene; Ethylbenzene; Organic packing material; Biodegradation

Khim Hoong Chu, Xiao Feng. *Enzymatic conversion of newspaper and office paper to fermentable sugars.* Pages 123-130.

Two types of waste paper materials, newspaper and office paper, were evaluated for their potential to be used as renewable feedstock for the production of fermentable sugars via the enzymatic hydrolysis of their cellulose fractions. The effects of four factors (hydrolysis time, enzyme loading, surfactant addition and phosphoric acid pretreatment) on the extent of sugar yield were assessed and quantified by using a methodical approach based on response surface methodology. The statistical experimental design used in this study requires fewer experimental runs compared to some commonly used experimental designs. In the newspaper hydrolysis case, response surface plots revealed that the degree of sugar release increased with an increase in hydrolysis time but it was hardly affected by the enzyme loading and acid pretreatment factors. The surfactant addition factor exhibited a positive effect when the enzyme loading level was relatively low. With office paper as the substrate, three of the four factors (hydrolysis time, enzyme loading and acid pretreatment) exhibited positive effects on the extent of sugar release. At local optimum conditions, the maximum sugar yield from office paper was found to be 0.82 g of reducing sugars per gram of paper, which was about 4.8 times higher than the maximum sugar release from the newspaper substrate.

- **Keywords:** Hydrolysis; Lignocellulosic; Optimization; Response surface; Waste paper

Aminul Islam, Yun Hin Taufiq-Yap, Chi-Ming Chu, Eng-Seng Chan, Pogaku Ravindra. *Studies on design of heterogeneous catalysts for biodiesel production.* Pages 131-144.

The production of biodiesel is gaining momentum with the ever increasing demand of the fuel. Presently, limited literature is available with respect to well designed solid heterogeneous catalyst for biodiesel production considering all the characteristics, process and operation parameters. Hence, a study was conducted to design effective heterogeneous catalyst for biodiesel production. Further, the significant impact of different catalysts, different feed stock, various reaction conditions such as temperature, methanol oil molar ratio, catalyst concentrations and stability/inactivation of the catalysts, are detailed out for transesterification process of biodiesel production. Based on the studies it can be concluded that well designed heterogeneous catalyst can yield high throughput of biodiesel.

- **Keywords:** Biodiesel; Transesterification; Heterogeneous catalyst; Feed stock

Chunjing Liu, Jia Liu, Jian Li, Hong He, Shujing Peng, Chao Li, Ying Chen. *Removal of H_2S by co-immobilized bacteria and fungi biocatalysts in a bio-trickling filter.* Pages 145-152.

Biological control of odor gases has gained more attention in recent years. In this study, removal performance of a vertical bio-trickling filter inoculated with bacteria and fungi was studied. Bacteria and fungi were isolated from activated sludge in a sewage treatment plant. By adopting "three step immobilization method", the bio-trickling filter could degrade pollutant immediately once hydrogen sulfide (H_2S) passed. The optimal empty bed resident time was 20 s. The optimal elimination capacity was about 60 g H_2S m^{-3} h^{-1} with removal efficiency of 95%. And the maximum elimination capacity was 170 g H_2S m^{-3} h^{-1}. Pressure drop was ranged between 5 and 15 mm H_2O per bed over the whole operation. Removal efficiency was not affected obviously after terminating nutrient supply. The bio-trickling filter could recover back after shut down H_2S gaseous and liquid supplies simultaneously. Microbial community structure in the bio-trickling filter was not changed significantly.

Combining bacteria and fungi would be a better choice for inoculation into a bio-trickling filter because of the quickly degradation of H_2S and rapid recovery under shut-down experiment. This is the first study attempting to combine bacteria and fungi for removal of H_2S in a bio-trickling filter.

- **Keywords:** H_2S; Bacteria; Fungi; Co-immobilization; Bio-trickling filter

Sang Joon Chung, Il Shik Moon. *An improved method of removal for high concentrations of NO by electro-scrubbing process.* Pages 153-158.

In the Ag(II)/Ag(I) redox mediator integrated scrubber system, NO reacts with the Ag(II) ions produced by the electrochemical oxidation of Ag(I) in an electrochemical cell present in the scrubbing solution (aqueous HNO_3 acid) to form NO_2. This NO_2 is then absorbed into the scrubbing solution and degraded to nitrate. Numerous experimental runs were carried out to evaluate the feasibility of the integrated system to treat industrial waste gases containing high NO*x* levels. The results showed that the levels of NO and NO*x* removal increased with increasing Ag(II) loading and contact time. Under optimized conditions, 93.5% and 73.3% of the NO and NO*x*, respectively, were removed by a single stage gas scrubber with 1.62 g L^{-1} Ag(II) operating at 25 °C and atmospheric pressure.

- **Keywords:** NO; NO*x*; Wet scrubber; Mediated electrochemical oxidation; Ag(I)/Ag(II) redox system