TECHNICAL SAFETY IN
UPSTREAM OIL AND GAS

“A Smörgåsbord of H₂S, Mercury and Design Safety”

KT Consortium AGM

Technical University of Denmark

www.genesisoilandgas.com
GENESIS… 29 YEARS OF FRONT END THINKING IN THE UPSTREAM O&G INDUSTRY

Create
Realise
Enhance

Specialist Technical Services
Specialist Capabilities
Proprietary Tools & Processes

Offer services across the Asset Lifecycle

Celebrated 25yr anniversary in 2013

Genesis Around the World:
15 locations, 850 personnel

Part of the Technip Group since 1999
Retained Independent Consultancy Role

150 personnel in central Aberdeen

Our Clients: many and varied
GENESIS ACTIVITIES ACROSS AN ASSET LIFECYCLE

- **CREATE**
  - Front end thinking
  - Field Development Planning
  - Concept Definition/Pre-FEED
  - Visualisation Studies
  - Reference Class Forecasting

- **REALISE**
  - Optimised engineering solutions
  - FEED
  - Detailed Design
  - Project Management Services

- **ENHANCE**
  - Protected, maximised value
  - Late Life Operation/Extension
  - Debottlenecking & Brownfield Modifications
  - Decommissioning & Restoration
  - Asset Integrity

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**SPECIALIST TECHNICAL SERVICES**

**PROPRIETARY TOOLS & PROCESSES**

**EXPERTISE**
Footnotes:

(1) Source: Public market quote from Bloomberg, LLP; Combination of market capitalization of FMC Technologies and Technip as of Jan 6, 2016; EUR/USD exchange rate of 1.05361 as of Jan 6, 2017.
(2) With four vessels under construction.
(3) Backlog as of Sep 30, 2016 (FMC Technologies: $3.02 billion; Technip: €12.28 billion), EUR/USD exchange rate of 1.09072 as of Oct 28, 2016; Source: individual company data as found in the European Prospectus filed on Jan 13, 2017.
(4) Revenue for full year 2015; Source: Form S-4 as filed with the SEC on Oct 25, 2016 and European Prospectus as filed on Jan 13, 2017.
YAMAL LNG, Siberia

Shell, Prelude, FLNG
H₂S PARTITIONING

- H₂S Creates Sour Gas / Oil
  - H₂S is Toxic / Corrosive
  - Levels often increase as a reservoir ages
  - Water injection carries Sulphur Reducing Bacteria

- Current trends in EOS use within Oil and Gas:
  - Peng-Robinson ’78 + Peneloux (95%)
  - CPA is gaining traction (MeOH partitioning studies in Genesis)

- Client engineers have tried using their current HYSYS model to estimate H₂S levels in offshore production
  - Standard HYSYS Peng-Robinson
  - Results do not match plant analysis

- Plant operators struggle to meet H₂S specifications in gas and oil export
  - Difficult to predict the effect of changes in well line-up
  - Production losses

- Some wells are very high water cut (80% w/w)
H₂S dissociates in aqueous phase
- \( H₂S ⇌ H^+ + HS^- \)
- \( HS^- ⇌ H^+ + S^{2-} \)
- Important for high water cut wells

Aspen ELECNRTL (C.-C. Chen)
- Gamma-Phi Approach
- Restricted to low pressures (< 20 barg)

<table>
<thead>
<tr>
<th>ID</th>
<th>Type</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equilibrium</td>
<td>HCL + WATER ⇌ CL- + H3O+</td>
</tr>
<tr>
<td>2</td>
<td>Equilibrium</td>
<td>WATER + HSO4- ⇌ H3O+ + SO4--</td>
</tr>
<tr>
<td>3</td>
<td>Equilibrium</td>
<td>H2SO4 + WATER ⇌ H3O+ + HSO4-</td>
</tr>
<tr>
<td>4</td>
<td>Equilibrium</td>
<td>WATER + HCO3- ⇌ CO3-- + H3O+</td>
</tr>
<tr>
<td>5</td>
<td>Equilibrium</td>
<td>2 WATER + CO2 ⇌ HCO3- + H3O+</td>
</tr>
<tr>
<td>6</td>
<td>Equilibrium</td>
<td>WATER + HS- ⇌ H3O+ + S--</td>
</tr>
<tr>
<td>7</td>
<td>Equilibrium</td>
<td>WATER + H2S ⇌ H3O+ + HS-</td>
</tr>
<tr>
<td>8</td>
<td>Equilibrium</td>
<td>2 WATER ⇌ OH- + H3O+</td>
</tr>
<tr>
<td>9</td>
<td>Dissociation</td>
<td>NA2SO4 → SO4-- + 2 NA+</td>
</tr>
<tr>
<td>10</td>
<td>Dissociation</td>
<td>NACL → CL- + NA+</td>
</tr>
</tbody>
</table>
OPPORTUNITY

- **CPA electrolyte model for H₂S**
  - Extend capability to high pressure unit operations

- Clients will usually have a process model developed
  - Significant investment to develop / validate
  - e.g. HYSYS, Pro II

- At present there is several years of delay before new models are implemented in commercial simulators
  - PC-SAFT is not available in HYSYS v8.8

- **KT Thermodynamics Engine**
  - CAPE-Open Compliant?
  - Plug-in to commercial simulators
  - License to end user
Mercury is a contaminant in many reservoir fluids, causing problems for:

• Safety of Personnel
• Process Integrity and Loss Prevention
• Environmental Emissions
• Product Export Specifications
• Equipment Contamination / Decommissioning (including the downstream supply chain)

Accurate well fluids analysis together with knowledge of how mercury will partition in the production processes are essential components for successful risk management.
Mercury is a natural contaminant in reservoir fluids.

Typical concentrations vary globally.

<table>
<thead>
<tr>
<th>Location</th>
<th>Natural Gas (mg/Sm³)</th>
<th>HC Liquids (ppbw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algeria (wellhead)</td>
<td>50-80</td>
<td>20-50</td>
</tr>
<tr>
<td>Groningen (wellhead)</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>North Germany (wellhead)</td>
<td>15-450</td>
<td>-</td>
</tr>
<tr>
<td>South Germany (wellhead)</td>
<td>&lt;0.1-0.3</td>
<td>-</td>
</tr>
<tr>
<td>South America</td>
<td>69-119</td>
<td>50-100</td>
</tr>
<tr>
<td>Far East</td>
<td>3-20</td>
<td>-</td>
</tr>
<tr>
<td>Far East</td>
<td>58-193</td>
<td>-</td>
</tr>
<tr>
<td>Far East</td>
<td>0.02-0.16</td>
<td>-</td>
</tr>
<tr>
<td>Africa</td>
<td>0.3-130</td>
<td>500-1000</td>
</tr>
<tr>
<td>Middle East</td>
<td>1-9</td>
<td>-</td>
</tr>
<tr>
<td>Eastern US Pipeline</td>
<td>0.019-0.44</td>
<td>-</td>
</tr>
<tr>
<td>Midwestern US Pipeline</td>
<td>0.001-0.10</td>
<td>-</td>
</tr>
<tr>
<td>North America</td>
<td>0.005-0.040</td>
<td>-</td>
</tr>
<tr>
<td>South America</td>
<td>69-119</td>
<td>-</td>
</tr>
<tr>
<td>Sumatra, Indonesia</td>
<td>200-300</td>
<td>-</td>
</tr>
<tr>
<td>Gulf of Thailand</td>
<td>100-1000+ (Note 1)</td>
<td>400-1200</td>
</tr>
<tr>
<td>Overthrust Belt (USA)</td>
<td>5-15</td>
<td>1-5</td>
</tr>
<tr>
<td>Oman</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Onshore Netherlands</td>
<td>180-200</td>
<td>-</td>
</tr>
<tr>
<td>Eastern Europe</td>
<td>1000-2000</td>
<td>-</td>
</tr>
<tr>
<td>Australia</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>Indonesia</td>
<td>250-300</td>
<td>-</td>
</tr>
</tbody>
</table>

Typical gas export pipeline specifications are around 0.01 µg/Sm³
Mercury and Mercury Compounds in Gas Processing

- Mercury may occur in different chemical forms:
  - Elemental Mercury (Hg₀)
  - Ionic
    - e.g. Mercuric Chloride (HgCl₂)
  - Inorganic
    - Mercury may react with chlorine, sulphur, and oxygen to form inorganic mercury compounds
    - e.g. Mercuric Sulphide (HgS
      solid
    ), naturally occurring mineral Cinnabar.
  - Organic
    - In condensates and petroleum liquids Mercury may react to form organo-metalic compounds.
    - e.g. Dimethyl mercury (CH₃)₂Hg
  - Speciation may change with Temperature, Pressure, pH and the chemical environment
  - Elemental mercury is often considered as the predominant form in natural gas processing
## Physical Properties of Elemental Mercury

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Hg</td>
<td></td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>200.59</td>
<td>kmol/kg</td>
</tr>
<tr>
<td>Density</td>
<td>13.53</td>
<td>Kg/m³</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>356.7</td>
<td>°C</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-38.9</td>
<td>°C</td>
</tr>
<tr>
<td>Solubility (water)</td>
<td>4.04E-9</td>
<td>mol frac 45</td>
</tr>
<tr>
<td></td>
<td>45 ppbw</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45 mg/m³</td>
<td></td>
</tr>
<tr>
<td>Solubility (pentane)</td>
<td>4.98E-7</td>
<td>mol frac 1385</td>
</tr>
<tr>
<td></td>
<td>868 ppbw</td>
<td></td>
</tr>
<tr>
<td></td>
<td>868 mg/m³</td>
<td></td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>1462</td>
<td>°C</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>1608</td>
<td>Bara</td>
</tr>
<tr>
<td>Critical Volume</td>
<td>0.035</td>
<td>m³/kmol</td>
</tr>
</tbody>
</table>
Advanced Mercury Modelling

• Genesis has developed a range of thermodynamic models for advanced applications:

• Genesis Mercury Modelling Software developed in ~2002
  – K factor approach
  – Accurately solves mercury mass balance for very low concentrations of mercury
  – (10^-9 to 10^-13 mol. frac.)

• Genesis Mercury (GEM) EOS developed in (2012):
Antoine Plot of Mercury Vapour Pressure Calculated using GEM EOS
Simplified Onshore Mercury Mapping Study

100% Hg

79% Hg

21% Hg

(Genesis EOS Model Integrated with Aspen HYSYS)
Mercury Mapping Using Aspen Plus

(Genesis EOS Model Integrated with Aspen Plus)
Mercury Mapping Using Aspen Plus

4 Phase Separator

Gibbs Flash Algorithm
Multi-Phase Equilibrium

Pure Hg Streams (Drop-Out)
Pipeline Adsorption Model – Discrete Sections

- Dynamic model of mercury adsorption and desorption in pipelines (and vessels)
- Assume that bulk gas phase is well mixed
- All mass transfer resistance is due to a stagnant boundary layer at the gas / pipe interface
- Adsorption / Desorption isotherms are fitted to estimate Hg adsorption equilibria
Pipeline Adsorption Model Indicative Results

- Mercury adsorption front profile along pipeline
- Mercury outlet concentration profile with time
- Time to mercury breakthrough
- Rate of mercury breakthrough and management strategy
• Experimental data for mercury is limited

• **GC-CPA**
  - make best use of limited data
  - $\text{Hg}^0$ functional group

• Include mercury species in Electrolyte CPA
PIPER ALPHA MEMORIAL STATUE, HAZELHEAD PARK, ABERDEEN, UK

DEDICATED TO
THE MEMORY OF THE
ONE HUNDRED AND SIXTY SEVEN MEN
WHO LOST THEIR LIVES
IN THE
PIPER ALPHA OIL PLATFORM DISASTER

6TH JULY 1988
LITERATURE REVIEW - PIPER ALPHA DISASTER

- Analysis by N. Renton, Operations Director, Genesis.
- Range of Sources used including Petrie Report, Cullen Report, Workshops and Published papers [Refs. 1-5].
- Main effort focused on Cullen Report.
- Cullen inquiry progressed in two parts;
  - The first to determine the causes and circumstances of the disaster;
  - The second to put forward recommendations for preventing something similar in the future;
- Report is in two volumes, 488 pages of evidence plus figures, tables, and plates.


UNDERVIEW OF EVENTS

- Failure event developed in 3 distinct stages
  - Preliminary leak / explosion
  - Escalation to oil separators
  - Escalation to Tartan and Claymore gas export risers

- Cause of initial gas / condensate leak
  - Failure within Permit To Work system
  - Start up of gas export compressor whilst undergoing maintenance
  - Gas leaked from temporary blanking flange
OVERVIEW OF PIPER ALPHA – PRODUCTION DECK LAYOUT
STAGE 1: CONDENSATE EXPLOSION 22:00

- Initial Leak occurred in **South East corner of Module C**.
- Leak lasted **30 seconds**.
- Total inventory released **30-80 kg** of hydrocarbon filling less than **25%** of the module.
- Ignition Source – Unknown, most likely **electrostatic discharge** from leak itself(*)..

**Deflagration**
- Maximum peak over-pressure **0.2-0.4 bar**

Section 5.103-5.109, pp68-69, [Ref. 1]

(*) Section 6.46, pg84, [Ref. 1]
STAGE 1: CONDENSATE EXPLOSION 22:00

Effects of the Initial Explosion in Module C……

- Destroyed the C/B Fire wall, parts of which disintegrated and became missiles.
- Missiles ruptured multiple oil pipework located 5ft away in Module B and potentially the 4” condensate line.
- Missiles also disabled the Deluge System – the fire pumps and deluge pipework in Modules B & C & D were most likely damaged beyond repair in initial explosion.
- Destroyed the wall of control room and devastated the people and equipment contained in it.
- Threw control room operator Mr Bollands 15ft across the room; blew Maintenance Lead Hand Mr Clark 6-8ft against computer terminals.
- Blew in 4 windows on the Lowlands Cavalier, 30m off the west face of Piper and blew chief engineer on the Lowland Cavalier from the deck into the bridge superstructure.
STAGE 2: OIL FIRE MODULE B – 15 SECONDS AFTER FIRST EXPLOSION (22:00:15)

- Generated temperatures in excess of 900 °C
- Extended into Module C
- ESV 208 was passing oil, allowing oil from wellheads to also feed fire.
- Oil (in huge quantities) ran down into 68ft Level, eventually causing pool fires next to horizontal sections of the Tartan and MCP-01 Gas Risers.
- Enough oil in the separators (50-55 tonnes) to sustain the fire for up to two hours (*) – the actions of Claymore and Tartan OIMs (in not shutting down oil export) likely to be irrelevant.

Sections 7.1-7.17, pp127-132, [Ref. 1]

Section 7.15, pg 131, [Ref. 1]
STAGE 2: OIL FIRE IN MODULES B, C & 68FT LEVEL (22:02)
RUPTURE OF TARTAN RISER (22:20)
STAGE 3 RUPTURE OF THE GAS RISERS (TARTAN 22:20; MCP-01 22:50)

- Full bore rupture of API 5LX-X60 Tartan Riser (120bar) directly upstream of ESV6 at 68ft Level.
- Inventory estimated at 18MMSCF.
- No PFP or Deluge (which had been disabled during Stage 1).
- Failure temp estimated at 580-700 ºC given 150 kW/m² pool fire underneath it.
- Full bore rupture of MCP-01 (120bar) at 22:50, 51MMSCF
- Structural failure began.
- Final failure of Claymore Gas Riser (62 bar) at 23:18.
- North-end collapsed by 00:15.
- Structural failure complete by 00:45.

Sections 7.18-7.24, pp132-134, [Ref. 1]
KEY LESSONS FOR PLANT DESIGN

- Location of hazards in relation to each other;
- Small leaks of gas (20-100kg) cause explosions capable of destroying pipework, vessels, and equipment (including safety systems);
- Design of Blast Walls;
- Location of control rooms relative to hazards;
- Location of safety systems in relation to hazards (e.g. redundancy of fire pumps);
- Riser location and protection (Passive Fire Protective Coatings).
QUANTITATIVE RISK ASSESSMENT (QRA) (PROBABILISTIC)

- Equipment Parts Count
  - Number of valves / Length of pipework
  - Leak frequency statistics

- Leak frequency distribution
  - Representative hole sizes (5, 10, 20, 50, 100, FB)
  - Geographical Location

- Hazard Consequence Modelling
  - Vapour cloud dispersion / flammability (CFD)
  - Thermal radiation intensity (DNV PHAST)
  - Explosion Overpressure / Drag Load (FLACS CFD)

- Scenario Assessment
  - Ignition probability and timing
  - Event trees

- Risk Metrics
  - Location Specific Risk (fatality per year)
  - Individual Risk Per Annum (fatality per year)
OPPORTUNITY - PSE APPROACH TO QRA

- QRA models are typically developed in Excel
  - Complexity due to large number of scenarios
  - Propose layout case and manually compare with base case

- QRA + Process Systems Engineering → Layout Optimisation
  - Risk Reduction as Constrained Optimisation problem
  - As Low As Reasonably Practicable (ALARP)
  - e.g. Equipment layout to minimise escalation risks
  - e.g. Optimum usage of Passive Fire Protection (PFP) coatings

- Phase Behaviour of Fluids Under Fire Relief

- Potential for Collaborations
  - Suppliers of Passive Fire Protection
  - Top Tier COMAH Sites / SEVESO III Directive
THANK YOU

Contact us
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