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CO_2 Safety and Transport

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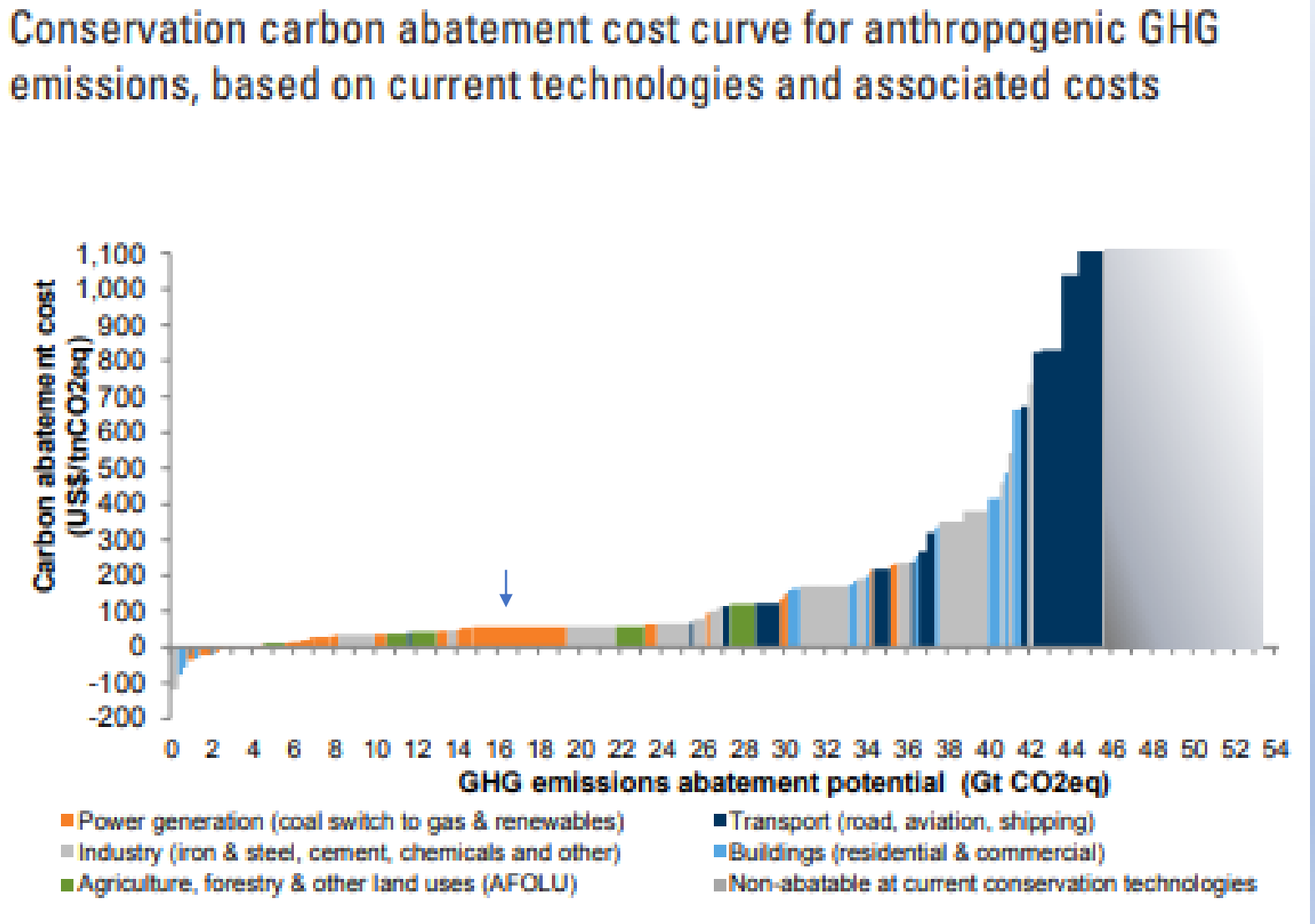
CO_2 abatement costs

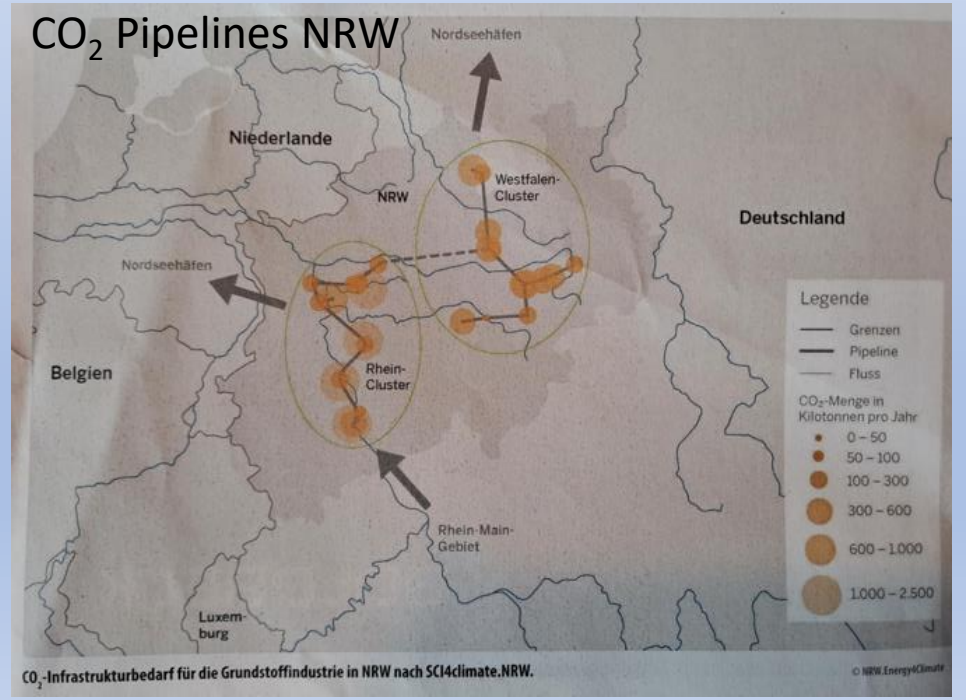


Source: Goldmann Sachs 2020

CO_2 ,in the center of the energy transition

- **CO_2 Capture, Storage, Transport:**
  - Capture from point sources, or directly from air
  - Storage, temporarily and permanent
  - Transport: pipelines, railcars, ships for **Millions of tons**
  - E.g. Germany 2023: National CO_2 Management Strategy

- **CO_2 project examples:**
  - PORTHOS CCS project Rotterdam, NL
  - KAIROS CCS project Antwerpen, BE
  - Carbfix CCS project, Iceland
  - OpenGrid pipeline to Wilhelmshaven, GE
  - Shell pipeline from NRW, GE to Rotterdam, NL
  - Victrol, Air Liquide: rail, ship infrastructures
    e.g. Duisburg harbor, GE

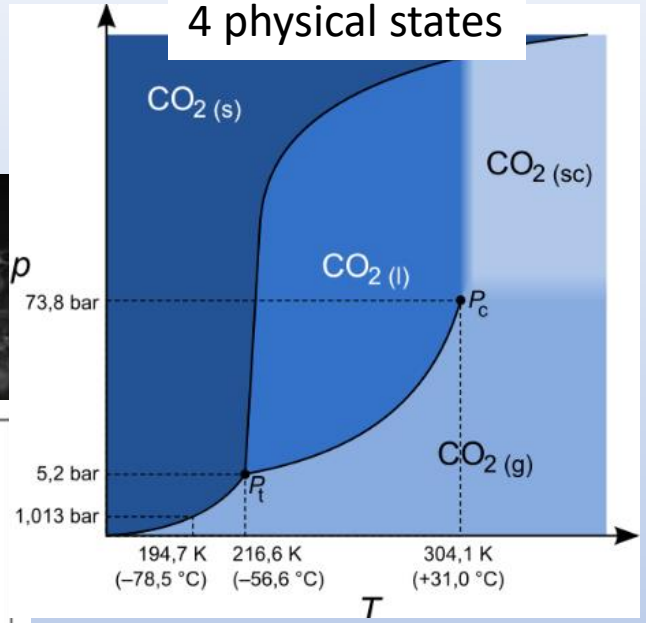


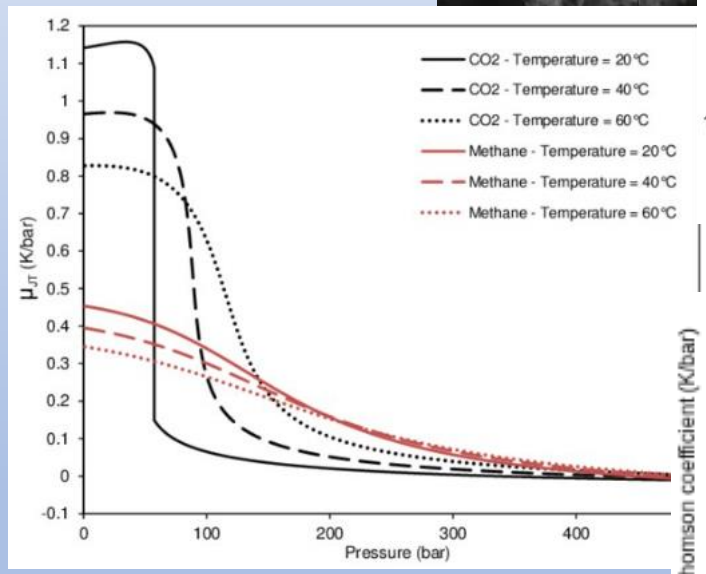
CO_2 Safety

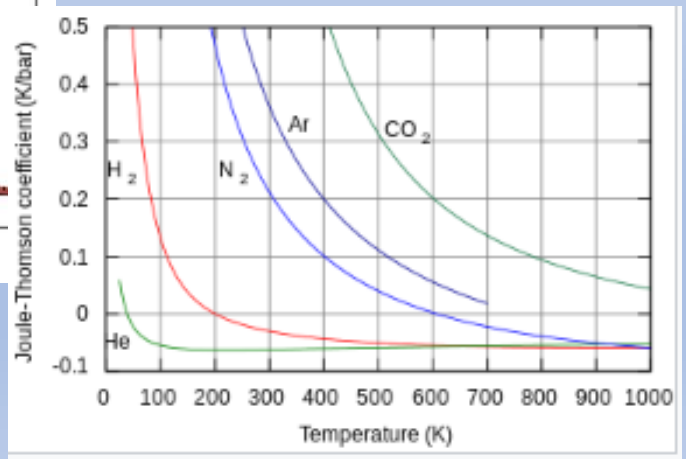
- CO_2 properties (physical & chemical) are well understood
  - Public Reports
- CO_2 is a trace component in the atmosphere (~ 420 ppm)
  - Necessary component for plant growth (>250 ppm) and keep Earth above freeze point (>200 ppm)
  - Average global Temp. increase $T = 3{,}1 \times \ln C/C_0$ with C0 = 290 ppm (1850-1900 pre-industr. conc.)
- CO_2 safety measures are well known
  - **Suffocation Hazard,** relevant with significant leaks of pipelines or in buildings
  - **Toxic** at elevated concentrations
    - 0,5 % 8 hr workplace concentration (= ~12 times the atmospheric content)
    - 2% Faster breathing, headaches
    - 5% Breathing difficulties, loss of consciousness
    - 8% Death within a few minutes
- Dry ice, fire extinguishing systems
  - Significant number of fatal accidents !

Physical & Chemical Properties of CO_2

- CO_2 sublimates (solid → gas)
  - No liquid state below 5,2 bar; at 20°C liquid only > 72 bar
  - Dry ice is solid CO_2 at -78,5 °C, which evaporates (sublimates)
- CO_2 is soluble in water, to an extent
  - 1 bar: at 20°C: 1,7 g/l (0,9 l CO2); at 0°C: 3,1 g/l
  - 5 bar: at 20°C: 8 g/l; at 0°C: 16 g/l
- CO_2 is heavier than air
  - Forms clouds, sinks to the ground
- CO_2 is an energy sink, not reactive
  - Inert gas under most conditions
- Strong positive Joule Thomson effect
  - CO2 heats up during compression (+1,1°C / bar)
  - CO2 cools down during expansion: Expansion from 50 to 1 bar: - 55°C (!)
    - **Relevant in pipeline leakages, where cooling can lead to embrittlement**

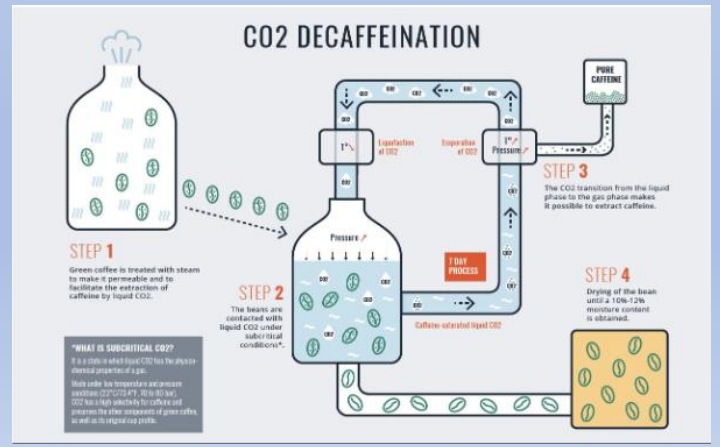






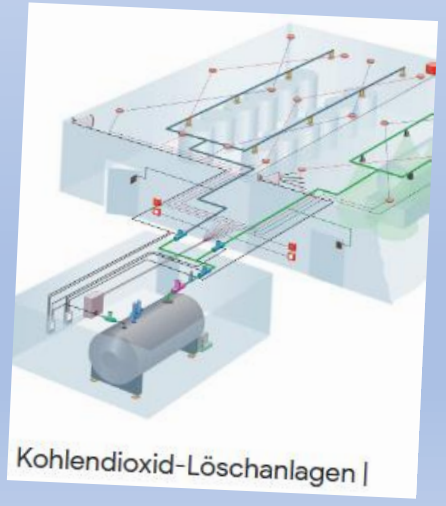
CCU: CO_2 is already used on industrial scale

- **Chemical synthesis**
  - Urea: $CO_2 + 2\ NH_3 \rightarrow H_2NCO_2^-\ NH_4^+ \leftrightarrow O=C(NH_2)_2 + H_2O$
    Ammonium Carbamate *Urea*
    - Worldwide production volume > 200 Million tons/year
  - Soda: $CO_2 + NaOH \rightarrow NaHCO_3 \rightarrow Na_2CO_3$ > 10 Million tons/year
  - Formamid ($HCO\text{-}NH_2$), Dimethylformamid, Salicylic acid (Phenol + CO_2)
  - Synthesis of specialty chemicals, Polyurethane Polyols, Diethylcarbonate, etc
  - Methanol: Future use in Methanol synthesis with green Hydrogen
    ($CO_2 + H_2 \rightarrow CO + H2O$ $CO + 2\ H_2 \rightarrow CH_3OH$) > 110 Million tons/year
- **Dry ice** (solid CO_2)
  - as coolant or for pressure blasting as cleaning method
- **Supercritical CO_2** as solvent and extraction agent
  - E.g. extraction of Coffein from coffee
  - Chemical cleaning of clothes
  - In oil drilling for tertiary oil recovery



CCU: CO_2 is already used on industrial scale

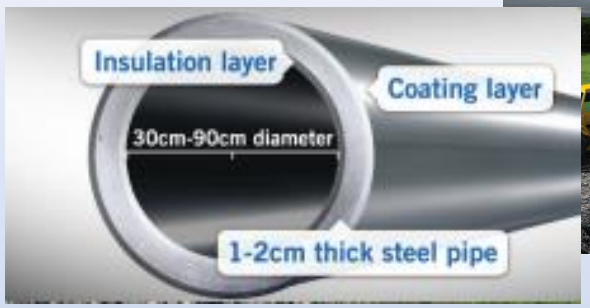
- Food additive
  - Carbonated drinks, baking
- Protective atmosphere in storage of fruits and vegetables
  - Delays the ripening process
- ‘Active’ welding gas
- Refrigerant R744
  - Automotive, supermarket air conditioning
- Fire extinguishing agent
  - CO_2 flooding of silos or buildings
  - CO_2 fire extinguishers



CO_2 transportation

- Ship
  - Quantities up to 1000 t are already transported by ship, typically food grade
  - Larger ships (40 to 100 kt) would be similar to LNG transports
- Railcars and trucks
  - CO_2 can be transported as a pressurized liquid
  - Quantities would not be sufficient to support CCS
- Pipelines
  - Large pipelines will be required for CCS. Some exist already or are under construction
  - CO_2 handled in pipelines as a pressurized supercritical fluid
- Dry ice
  - Only small quantities

CO_2 transportation



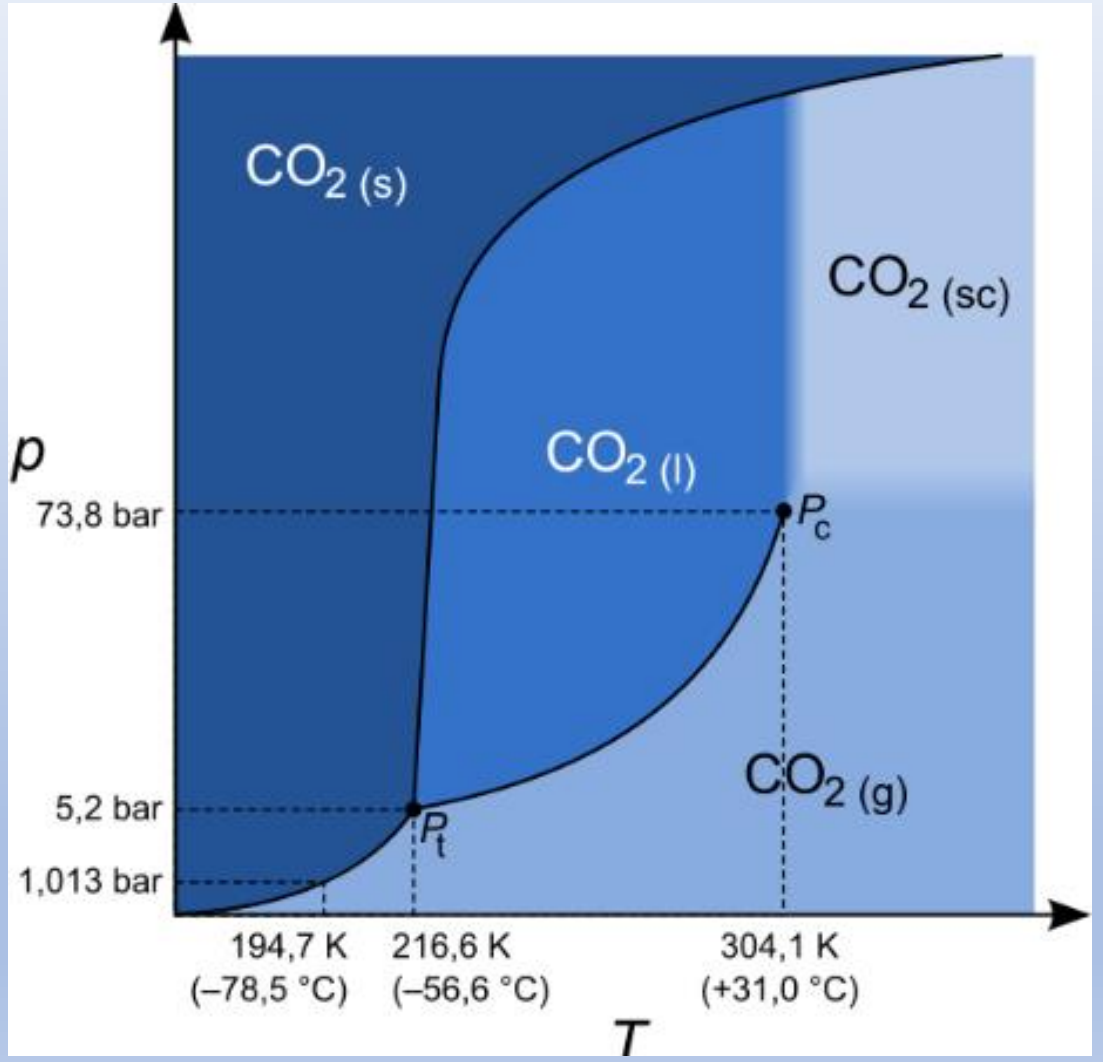
- **Pipelines**
  - Thousands of km of existing pipelines
  - US: ~50 pipelines, 6500 km, 70 Million t /yr
  - Typical transport conditions: **super critical state** (T_k= 31 °C, P_k= 74 bar)
    30 – 40 °C, 90-120 bar, density ~800 kg/m3, viscosity 0,08 cSt (mm2/s)
  - For toxicity and corrosion reasons, **H_2S** and **SO_2** must be kept **below a few hundred ppm** each
    - H_2S and SO_2 impurities can cause stress corrosion cracking
  - Pipeline materials of construction: Carbon steel (dry) or Ni alloy 304L/1.4341 (wet)
    - CO_2 must be dried (dehydrated) to control corrosion and to avoid hydrates at low temperatures
    - Temperatures can fall to – 20°C → Consider cold brittleness if carbon steel is used
    - Temperature during depressurization may reach – 78°C !
      - Relevant in pipeline leaks, where fog and ice can form from cold CO_2
  - **Excavation is the most frequent cause of pipeline rupture**
  - The bigger the pipeline, the less likely are leaks (e.g. all 24” pipelines: 1 leak per 50 000 km /yr)

Pipeline design codes for CO_2

- CO_2 in European standard EN 14161: class C fluid (similar to N2, Ar, Air)
- CO_2 in American standard ASME B31.4/31.8: hazardous fluid (similar to N2, Ar, Air)

Phase Diagram of CO_2

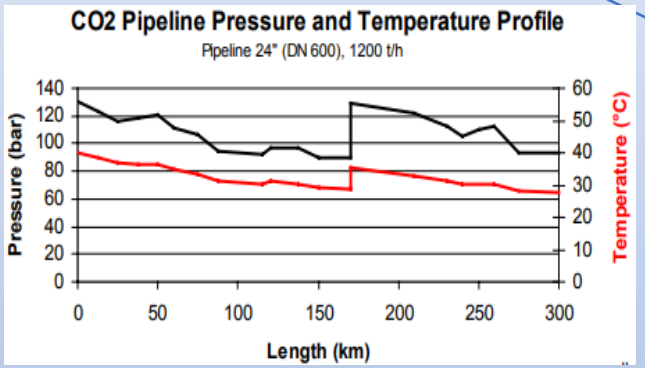
- CO_2 sublimates
  - No liquid state below 5,2 bar
  - At ambient temperature liquid only above 72 bar

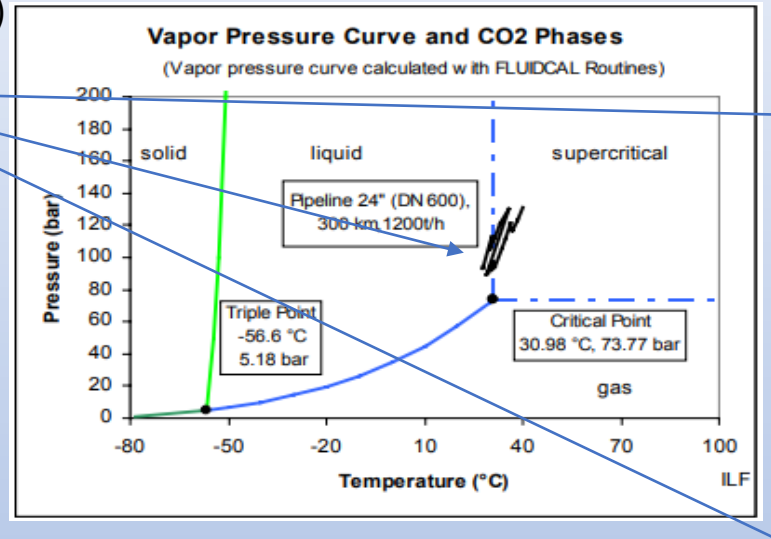


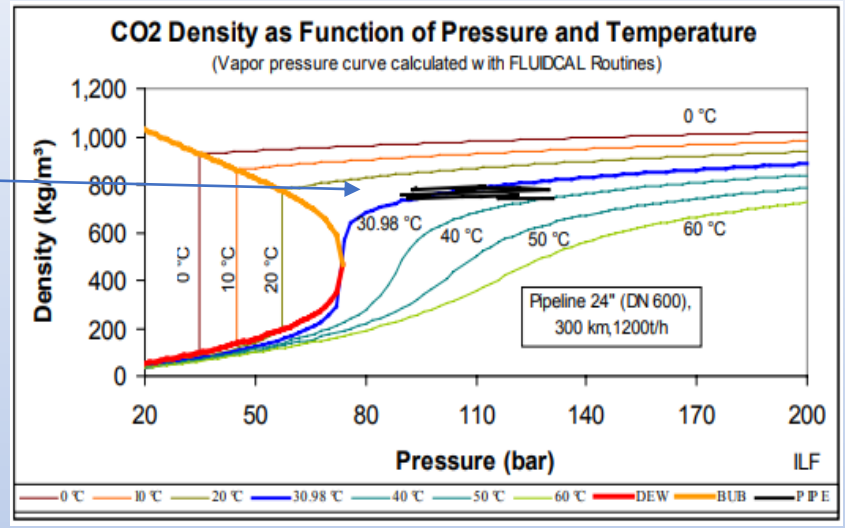
CO_2 transportation conditions in pipelines

- Example: 24” Pipeline, 300km, 1200 t/hr
  (Kaufmann, 2008, Pipeline Tech. Conf.)

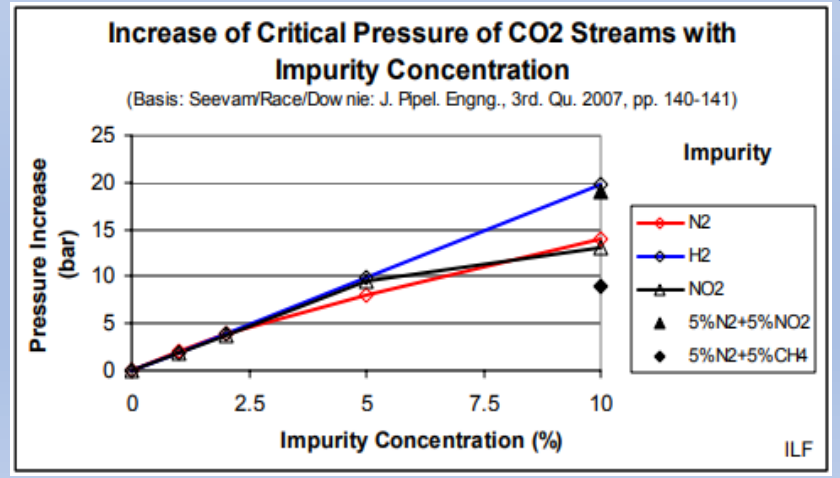
Operating window

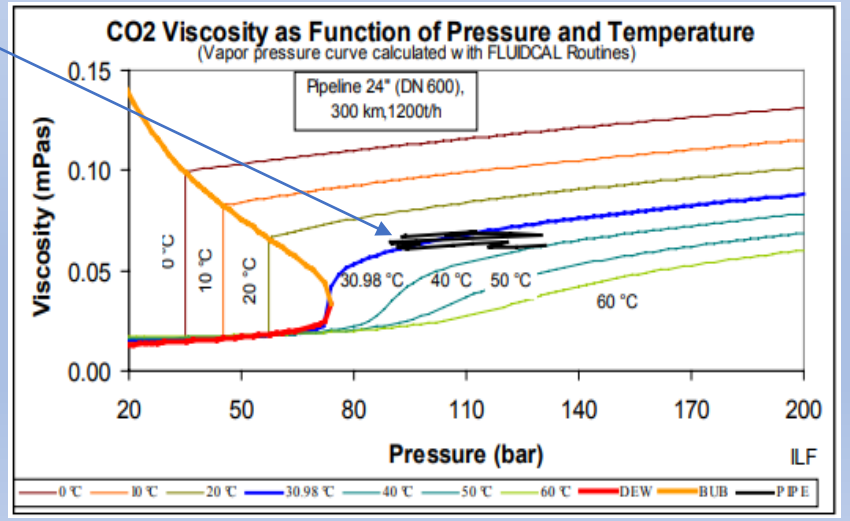






3 to 7 compression stages

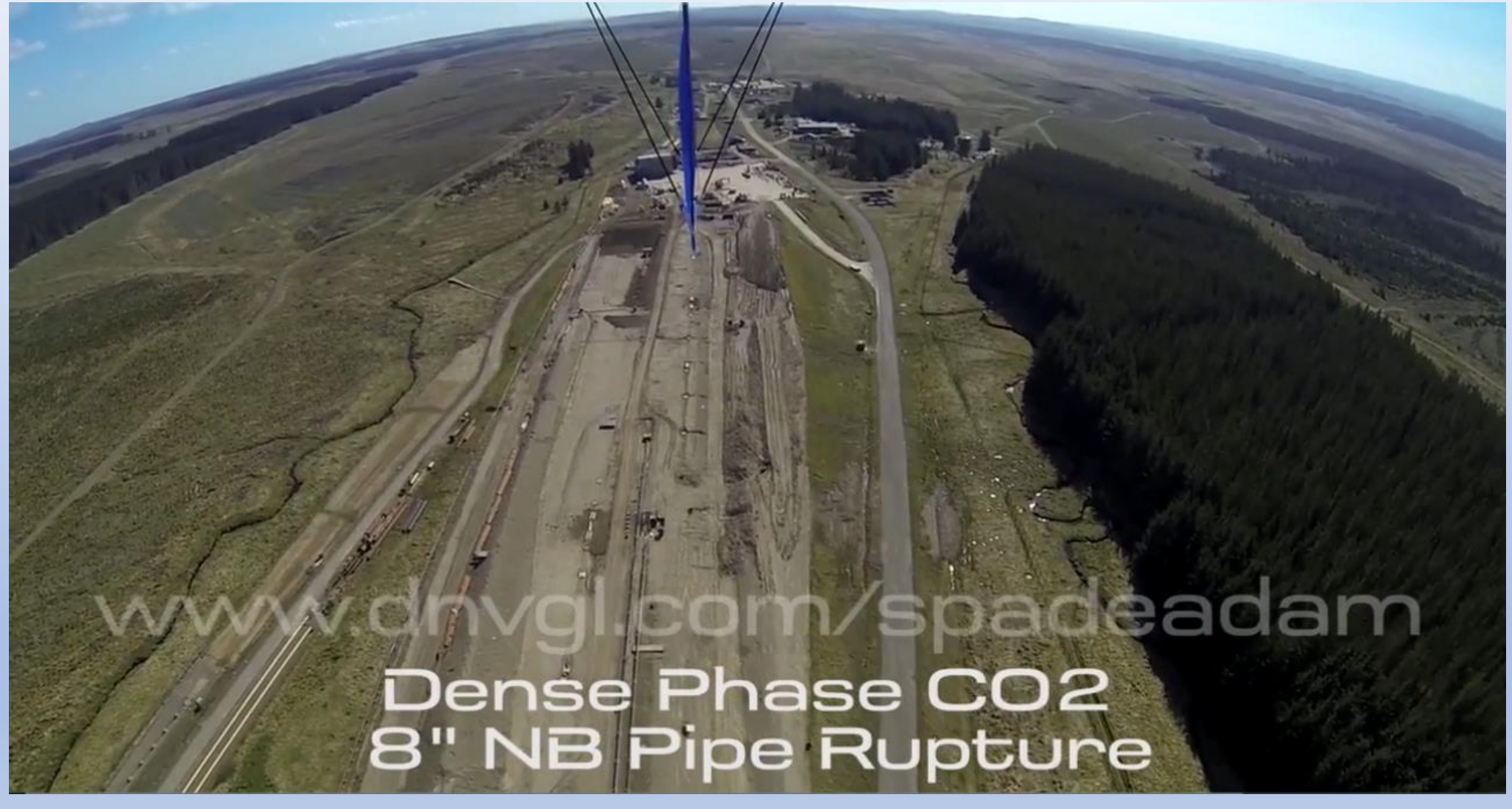




Rupture of CO2 pipeline, video

Dense phase CO2 8" NB pipe rupture video - DNV

Rupture of CO2 pipeline, video (DNV)



Accidents with CO_2

Fatal accidents with geological CO_2 releases

- **1979, Dieng, Indonesia:**

  Release of 200 000 t of CO_2 prior to a volcanic eruption.
  The cloud flowed to the plain below, and suffocated 142 people

- Natural release of CO_2 in some areas in Italy has lead to fatalities of animals and humans

Accidents with CO_2

Fatal accidents with geological CO_2 releases

- On 21 August 1986, a limnic eruption at **Lake Nyos** in northwestern Cameroon killed 1,746 people and 3,500 livestock.[1]
- Sudden release of between 300,000 and 1 Million tons of CO_2. The gas cloud initially rose at 25 m/s and then, being heavier than air, descended onto nearby villages, displacing all the air and suffocating people and livestock within 25 kilometres of the lake.

- A **limnic eruption**, also known as a **lake overturn**, is a very rare type of natural disaster in which dissolved CO_2 suddenly erupts from deep lake waters, forming a gas cloud capable of suffocating wildlife, livestock, and humans.
- Much larger lake Kivu (Kongo, Ruanda) has limnic eruptions every ~1000 years
- Messel pit fossil site, Germany, believed to originate from a limnic eruption
- More details e.g. Wikipedia article

Accidents with CO_2

Fire extinguishing systems

2020: Ten people have died and 19 were injured after high concentrations of carbon dioxide began to leak from the fire extinguishing system on a cargo ship in China.

Mönchengladbach (RPO). Unfall in einer Lackfabrik in Mönchengladbach. Aufgrund eines technischen Defektes einer Löschanlage sei eine große CO2-Menge frei geworden, sagt ein Polizeisprecher auf Anfrage unserer Redaktion. Die Polizei meldet bislang 107 Verletzte, davon sind 16 schwer verletzt.

- Ein paar Sägespäne waren am Samstag Morgen in Brand geraten, die Löschanlange sprang an, CO2 strömte aus und erstickte den Brand, Fall erledigt, kein nennenswerter Sachschaden.
- Leider schaltete sich die Löschanlange nicht wieder aus und das Kohlendioxid reicherte sich in der der Umgebung an, die Fabrik liegt in einer Senke.
- Anwohner wollten wegfahren, die Motoren hatten nicht genügend Sauerstoff, die Fahrer wurden ohnmächtig. Es müssen unheimliche Szenen gewesen sein.
- Die Rettungskräfte sorgten mit großen Ventilatoren in Form von über dem Gebiet kreisenden Helikoptern für eine bessere Durchlüftung der Senke mit Sauerstoff.
- Keller der Häuser wurden mit großen Gebläsen belüftet und die Situation ist mittlerweile wieder halbwegs normalisiert.
- Zum Glück ist niemand gestorben, “nur” ein Retter liegt noch auf Intensivstation.

CO_2 Safety Recommendations (CCU, CCS)

- Be aware of physical and chemical properties !
- Apply same management and processes as for other chemical hazards
- Establish a Process Safety Management System, if it does not exist yet
  - Thorough Safety reviews during design/project phase, ensure high expertise
  - Periodic review of safety concept during the operation life of the installations
  - Establish a Management of Change (MoC) process
- Inspections, RBI program to ensure asset integrity and reliability
- Have an Emergency plan (internal and external) and keep it up to date, practice regularly
  - Involve the communities which could be affected
- Exchange information on reliability and safety with other players in the same industry
  - Establish a continuous learning process from this