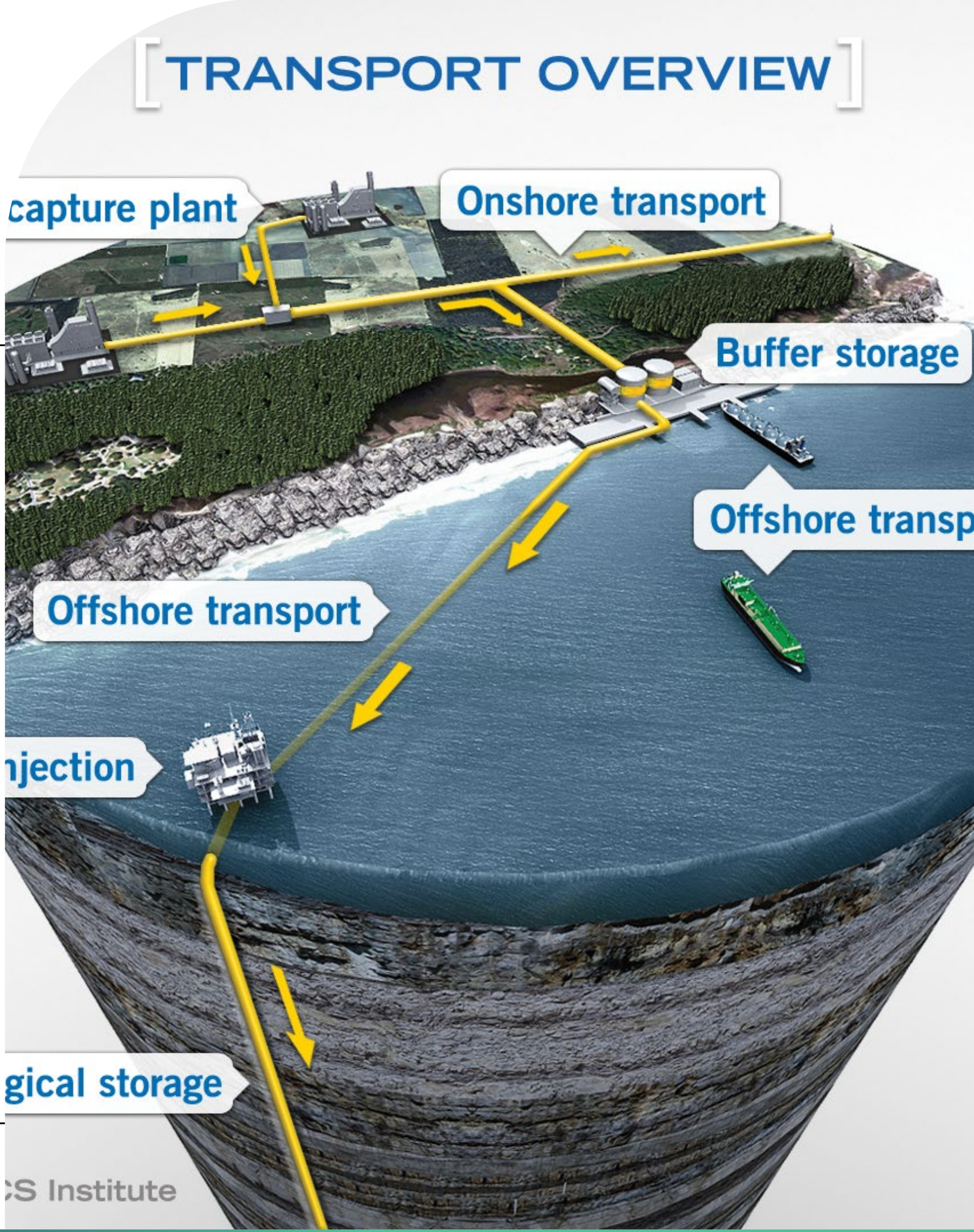
Odorization technology

For improved CO_2 onshore transport safety

Pipeline Safety Research and Development Forum 2023



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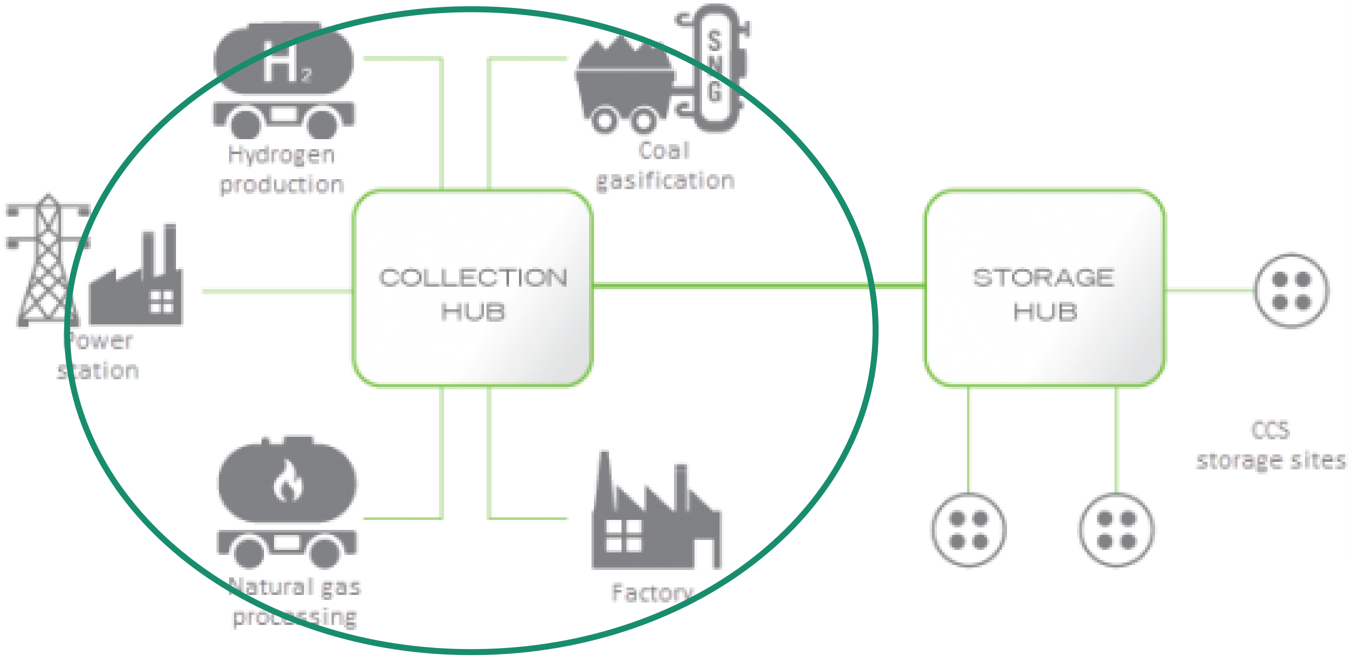
CARBON NEUTRALITY OBJECTIVES AND CARBON CAPTURE

→ IPCC scenario 1,5° : toward Carbon Neutrality

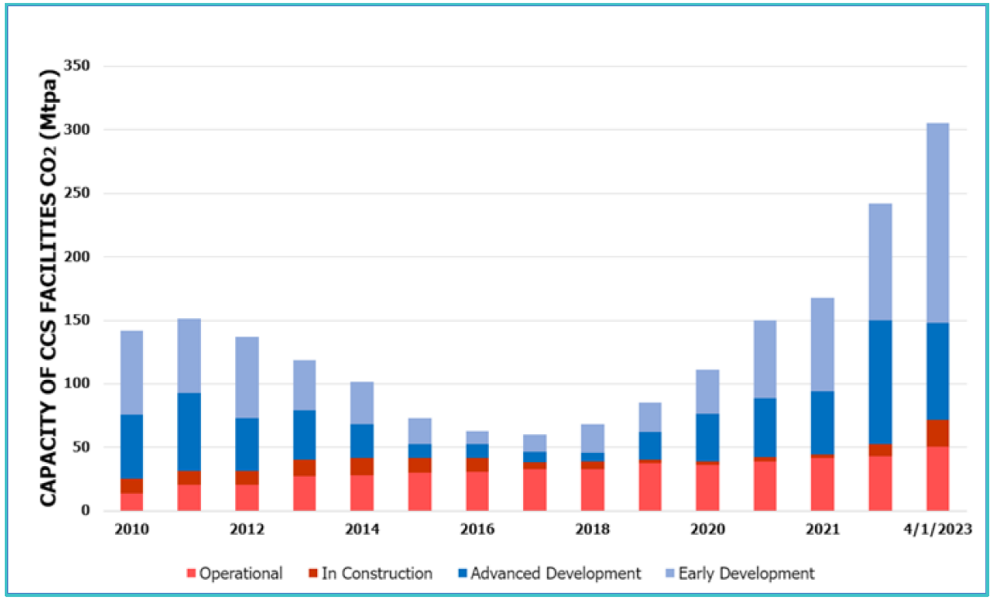
	2020	→	2050
Emission CO_2	~40Gt/y	→	~6 Gt/y
Absorption CO_2	~0 Gt/y	→	~6 Gt/y

Need for increase development of Carbon reduction initiatives such as CCUS



CARBON NEUTRALITY OBJECTIVES AND CARBON CAPTURE

PIPELINE OF COMMERCIAL CCS FACILITIES BY CAPTURE CAPACITY



The capture capacity of facilities excludes:

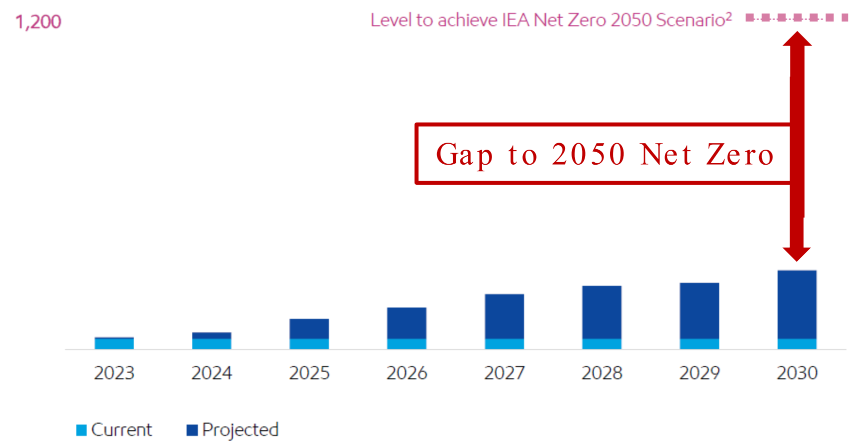
- Transport and storage-only facilities
- Suspended operations
- Announced facilities

Data through 1 April 2023

Global CCS institute data

But more industry progress is needed to meet societal emissions goals

Global CCS industry capacity and project pipeline trends[1], MTA



Only ~**50 MTA** of CCS capacity is operational today.

If all projects proceed, society will experience a **7x** growth rate through 2030 but will be **3x** short of the pathway needed to achieve IEA Net Zero Emissions 2050 Scenario.

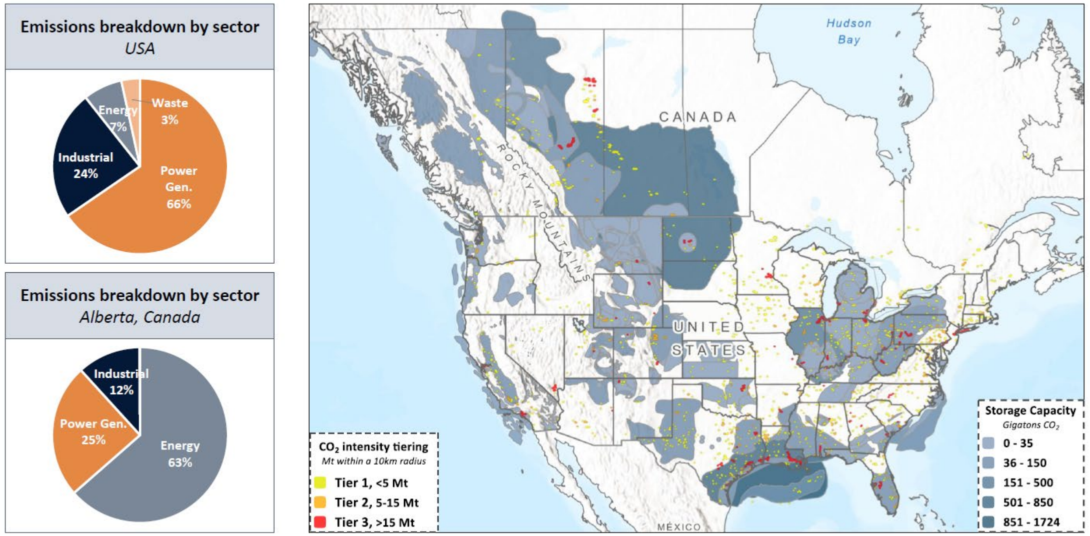
We need to identify enablers for exponential acceleration.

ExxonMobil *1. CCS Project data based on Wood MacKenzie, 1Q23 CCUS Market Tracker | 2. IEA World Energy Outlook 2022*

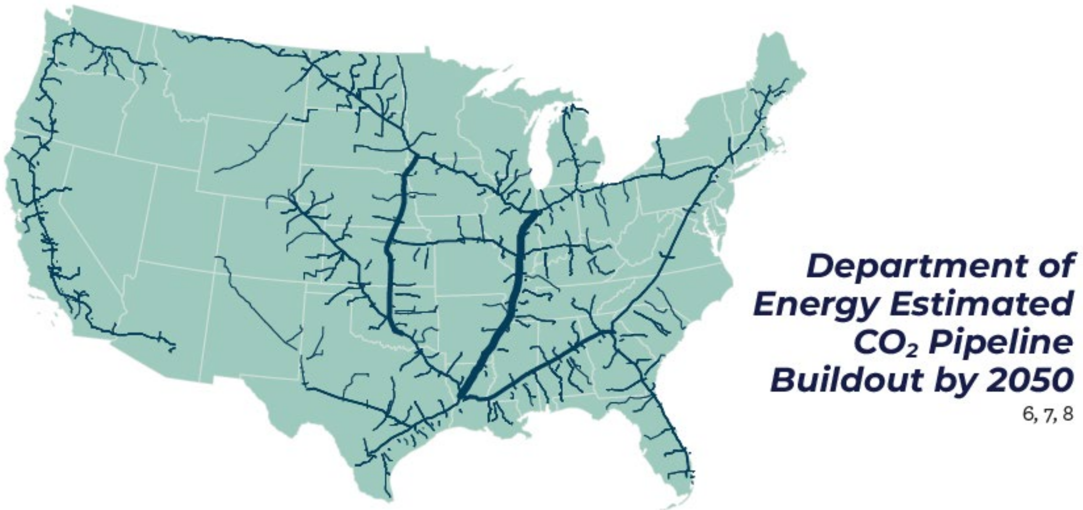
CCUS DEVELOPMENT CONSEQUENCES

→ Developping infrastructure for Capture, Transport and Storage in wide variety of regions in NA to connect large emitters (Oil/ Energy / Agro / Ethanol/ Steel/ Cement) to storage locations

CCUS is potentially as important to the 10 years as shale and LNG have been to the last 10 years



Source: Rystad Energy CCUS Dashboard, May 2023



→ CO_2 transportation will cease to remain limited to « remote locations » and « short distance » direct injection for EOR to be closer to population.

→ Increase of CO_2 transportation associated risks (corrosion, leakage, asphyxiation)

INCREASED RISKS OF ACCIDENTS SUCH AS THIS ONE

Feb 2020: GeoHazard → pipeline rupture, 350 m³ liquid CO_2 released (**385 mt**), vaporized and plume heading to Satartia town : 49 people injured (intoxication) and 250 people evacuated

Figure 2: Vehicle is Parked on HWY 433 - The White is Ice Generated by the Release of CO_2 - The Blue Arrow Points North (Aerial Drone Photograph Courtesy of the Mississippi Emergency Management Agency)

Figure 6: Topographical Map Showing the Delhi Pipeline (Green) and Denbury's Buffer Zone (Red) on Either Side of the Pipeline and the Proximity to Satartia (Blue Star Indicates the Rupture Site)

Odorized CO_2 due to presence of H_2S and other impurities (geological source of CO_2) → enabled detection by public even though the cloud had moved away from pipeline

Odorization technology

INTRODUCTION TO ODORIZATION TECHNOLOGY AS APPLIED TO NATURAL GAS

→ **Why odorization**: to detect leakages for dangerous odorless gases/liquids to protect the population against leakage consequences

→ **Odorant characteristics** (cf ISO 13734):

- Strong odor at low concentration
- **Distinctive « gassy » smell**
- Non toxic
- Stable during storage and use with gas/liquid to be odorized

Main odorants used for natural gas:

- Europe/China/Maghreb/Singapore: Pure THT
- Americas/Middle East/Australia: TBM based blends
- EM not used but may be naturally present in nat gas

Main odorants used for LPG: EM

Table A.1 - List of chemical and physical properties of pure sulphur compounds

Sulfur compound	Formula	Molar mass g/mol	Boiling point °C	Freezing point °C	Density (at 20 °C) g/cm³
Sulfides (thioether)					
Dimethyl sulfide (DMS)	CH_3SCH_3	62,14	37,3	-98,3	0,848 3
Methyl ethyl sulfide (MES)	$CH_3SC_2H_5$	76,16	66,7	-105,9	0,842 2
Diethyl sulfide (DES)	$(C_2H_5)_2S$	90,19	92,1	-103,9	0,836 2
Tetrahydrothiophene (THT)	C_4H_8S	88,17	121,0	-96,1	0,998 7
Mercaptans (thiols)					
Methylmercaptan (MM)[a] (methanethiol)	CH_3SH	48,11	5,9	-123	0,866 5
Ethylmercaptan (EM)[a] (ethanethiol)	C_2H_5SH	62,14	35,1	-147,8	0,831 5[b]
n-Propylmercaptan (NPM) (1-propanethiol)	C_3H_7SH	76,16	67 to 68	-113,3	0,841 1
iso-Propylmercaptan (IPM) (2-propanethiol)	$(CH_3)_2CHSH$	76,16	52,6	-130,5	0,814 3
n-Butylmercaptan (NBM) (1-butanethiol)	C_4H_9SH	90,19	98,5	-115,7	0,841 6
sec.-Butylmercaptan (SBM) (2-butanethiol)	$CH_3CH(SH)C_2H_5$	90,19	85	-165	0,829 5
iso-Butylmercaptan (IBM) (2-methylpropane-1-thiol)	$(CH_3)_2CHCH_2SH$	90,19	88,5	< -70	0,835 7
tert.-Butylmercaptan (TBM) (2-methylpropane-2-thiol)	$(CH_3)_3CSH$	90,19	64,3	-0,5	0,794 3[b]

Values taken from the *Handbook of Chemistry and Physics*, 87th ed., CRC Press, Boca Raton, Florida, USA.

SAFETY APPROACH

→ Odorants are mainly used for flammable gases/liquids

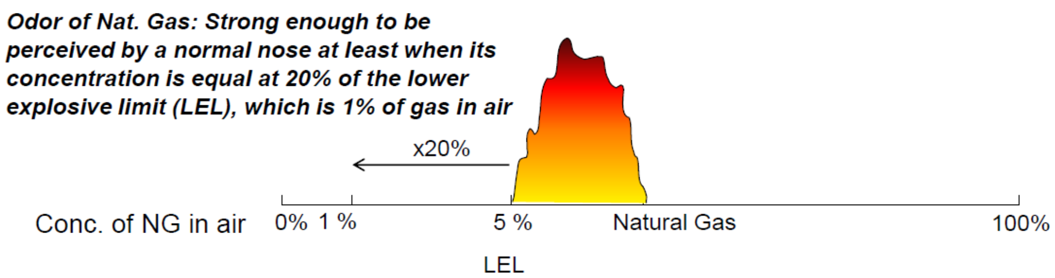
SAFETY APPROACH

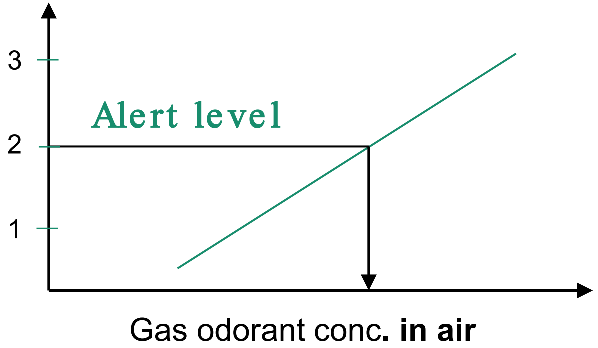
Alert at 20% of LEL

Which odorant concentration?

→ Intensity curves are established for each odorant blend (by trained people) according to a referenced method.

→ Definition of a concentration allowing non trained people **to smell and to identify** the odor with a simple sniff (Sales scale level 2)



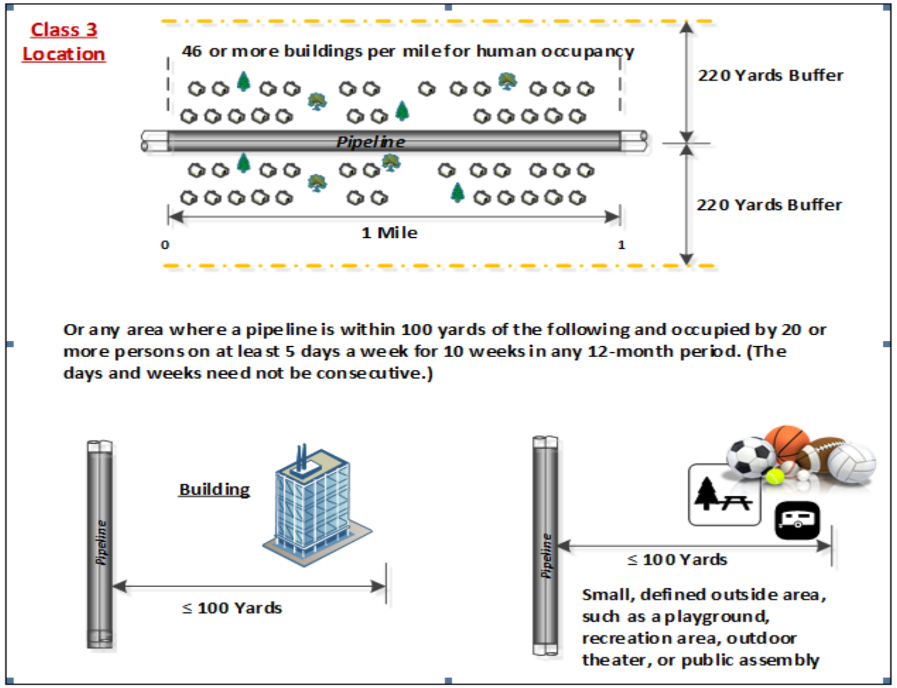


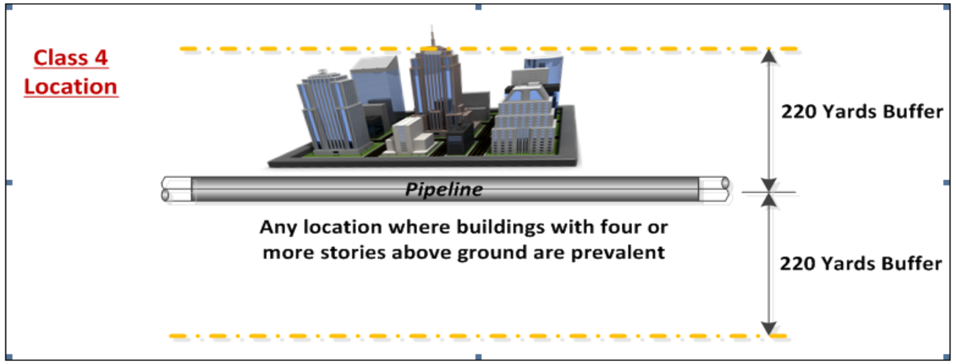
US REGULATORY REQUIREMENT: IN POPULATED AREAS

→ Natural Gas Pipeline Safety Act issued 1968:

→ Enabled DOT- PHMSA to establish **49 CFR Part 192** in 1970, including the odorization requirements for distribution and transmission networks in **§192.625**

→ American Gas Association (**AGA**) **Odorization Manual**: describes the pipeline classification





→ **Odorization** being only required in **Distribution** and **Transmission class 3 & 4 pipelines**

ODORIZATION EFFICIENCY: CASE STUDY FOR FRANCE

→ Efficient odorization program enables about 28 000 calls* for gas leakages per anum, enabling quick repairs and preventing as many gas accumulation situations.

- ~ 38 000 km (*23 000 miles*) high pressure natural gas transmission pipelines

\+

- > 200 000 km (*124 000 miles*) natural gas distribution network

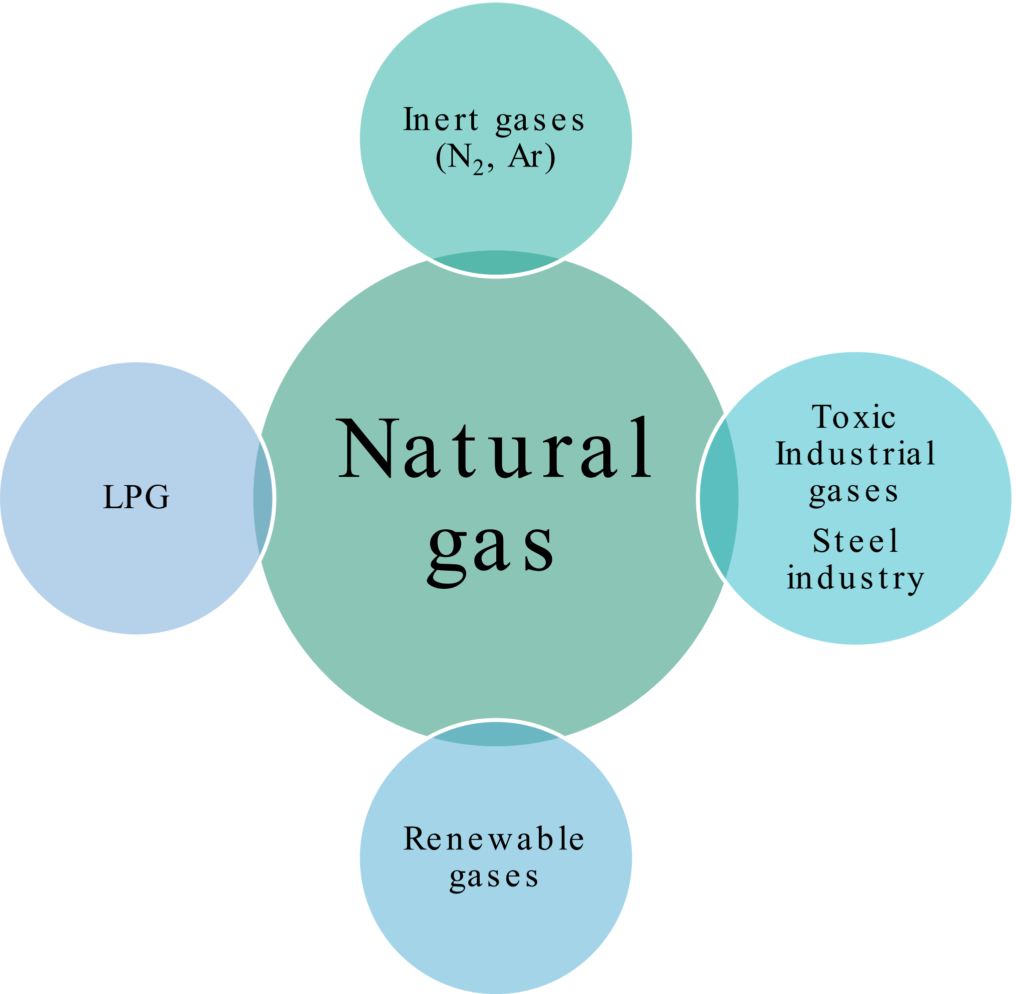
> 150 000 miles all odorized using the same technology: TetraHydroThiophene

DIRECTION GÉNÉRALE
DE LA SÉCURITÉ CIVILE
ET DE LA GESTION DES CRISES

* 2020 figures

Odorization Technology Transferrability

ODORIZATION TECHNOLOGY TRANSFER : CASE STUDIES



Gas source	O_2	CO	H_2	CO_2	N_2
BFG	0,4%	20-36%	1,5-8%	3,5-13%	55-61%
LDG	traces	65-80%	-	5-7%	A little

METHODOLOGY: EXEMPLE OF STEEL GASES

RISK BASED EVALUATION

Definition of highest tolerated exposure considering gas composition and associated risks.

- *Toxicity risk of CO achieved before flammability and asphyxiation risks (few hundreds ppm CO)*

→ *ALERT dosage determined to warn people before toxic exposure (STEL 300 ppm)*

Looking for traces → need for high intensity odorant

TECHNOLOGY PROPOSAL ACCORDING TO SCENARIO (evaluation of fading potential)

→ Evaluation of Gas purity: presence of deleterious impurities, condensates, water, dusts.

Presence of dusts and water saturated

→ Evaluation of potential technical barriers: compatibility of end use with sulfur traces

No influence on steel surface, limited SOx emissions

→ Evaluation of process conditions: pressure, temperature, flowrate, pipe network material section and lenght

Short carbon steel networks at low pressure and high flowrates at ambiant temperature

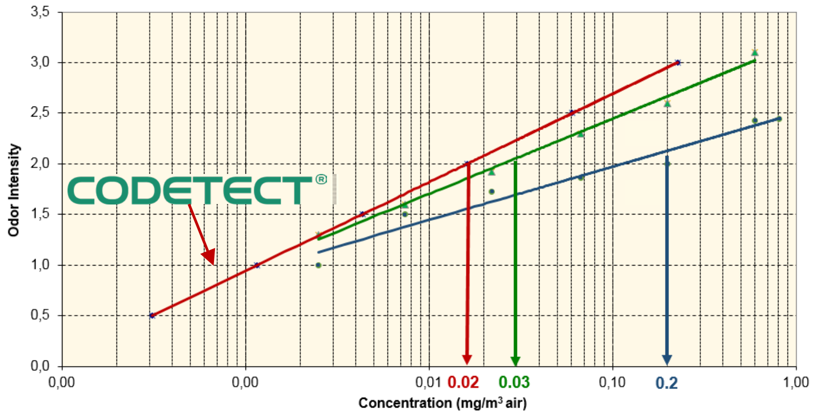
METHODOLOGY: EXEMPLE OF STEEL GASES

ARKEMA TECHNOLOGY PROPOSAL:

Proprietary mercaptan / sulfide formulation with properties enabling low reactivity, high intensity, easy regasification after adsorption on surface or into condensates:

CODETECT®

DETERMINATION OF ODOR INTENSITY CURVE



PILOTING

Field evaluation: piloting in steel industry on BFG (20-30% CO) to assess odorization efficiency

IMPLEMENTATION

Field implementation in China to improve safety around LDG networks (65-80% CO)

EVOLUTION OF CO_2 TRANSPORTATION NETWORK

→ Existing CO_2 onshore transport for Enhanced Oil Recovery (EOR), but mainly in **remote areas** (eg Canada Quest) / over **short distances**

→ With CCS more CO_2 will have to be transported onshore **through long distances** in **populated regions**

CO_2 **PIPELINE** MILEAGE AND REGULATIONS

CO_2 leakage risk in populated areas

→ Toxicity by Oxygen displacement

STEL = 30 000 ppm

Considering a Safety factor → 20 to 50% STEL

→ **We could aim 6 000 - 15 000 ppm CO_2**

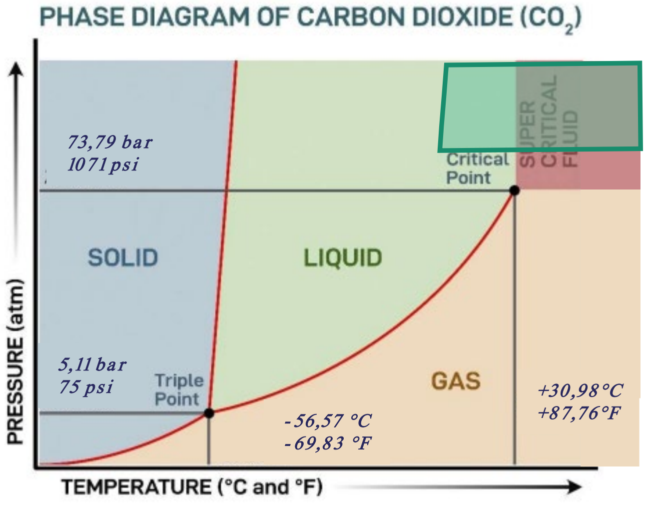
Transport conditions:

→ Gas phase

→ Dense phase (supercritical or liquid)

Supercritical : pressure and temperature above critical point

→ Transport phase determined by optimization of transport costs (pressure drop)



Max throughput:

Dense phase:

Pressure >74 bar (1071 psi)

ODORIZATION TECHNOLOGY TRANSFER FOR CO_2 TRANSPORT

Pipeline conditions (Material, P, T) are acceptable with respect to odorant and current equipment used for injection in HP Transmission networks.

- Odorant **currently injected in up to 90 bars** (1300psi) pipelines in France. And **up to 250 bars** (3600psi) for CNG stations.

- Odorant should be **fully injectable down to -45°C** (-50°F) (NA Winter season)

They display **much lower freezing point** and ppm level water content resulting in **extremely low "cloud point"** *(temperature at which free water traces separate and crystallize)*

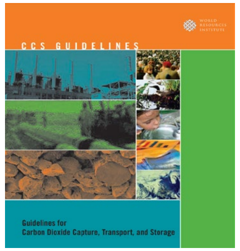
- Compatibility of the S-based odorant with usual pipeline material is already proven (**no corrosion issue**).

refer to : ISO 13734 requirements

Odorants were already recommended to be considered in case of populated areas in 2008

(establishment of this report)

http://pdf.wri.org/ccs_guidelines.pdf



Satartia accident lessons:

Sulfur-based impurities in CO_2 stream can effectively odorize

Targeting specific odorant would bring benefits:

Standardized practice (Stability & Efficiency of odorant)

Improved Safety for population

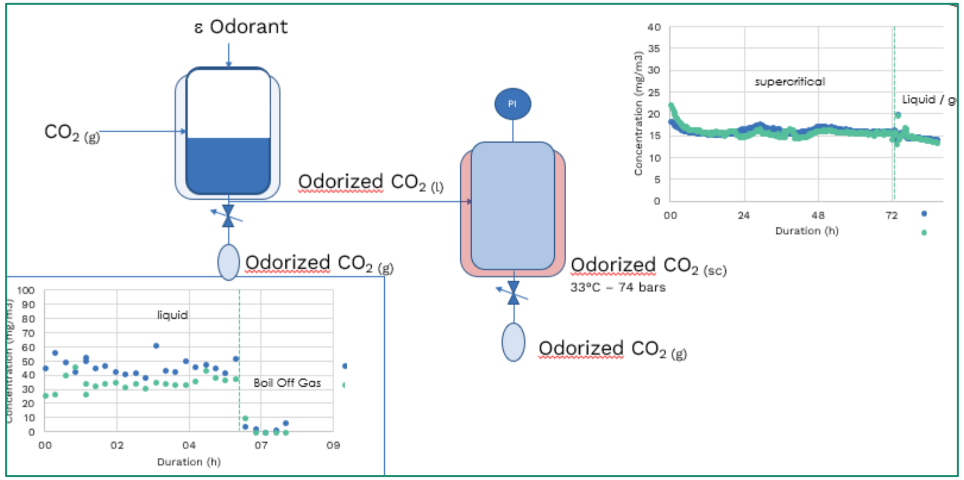
R&D TO MEET CCS DEVELOPMENT NEEDS FOR IMPROVED SAFETY

Technical feasibility evaluated under various conditions with pure CO_2

Lab evaluation performed
Arkema odorant R&D – Lacq – France

Gaseous CO_2 odorization (***Pure***), liquefaction, and leak simulation from:

- Gas
- Liquid
- Supercritical state



Impact of CO_2 impurity profile on technology selection

Intensity / odor character / stability

Example of some European projects spec

Purity from > 91 % to > 96 %

Some impurities tracked down to ppm, other to % levels.

CO_2 specifications from different projects & operators						
			ARAMIS [3]		National Grid [4]	
	Northern Lights [1]	PORTHOS [2]	Shipping	Pipelines	Dense Phase	Gas Phase
CO_2	Balance	≥ 95% mol	Balance	≥ 95% mol	≥ 96% mol	≥ 91% mol
H_2O	≤ 30 ppm	≤ 70 ppm	≤ 30 ppm	≤ 70 ppm	≤ 50 ppm_v	≤ 50 ppm_v
O_2	≤ 10 ppm	≤ 40 ppm	≤ 10 ppm	≤ 40 ppm	≤ 10 ppm_v	≤ 10 ppm_v
NO_x	≤ 10 ppm	≤ 5 ppm	≤ 1.5 ppm	≤ 2.5 ppm	≤ 100 ppm_v	≤ 100 ppmv
SO_x	≤ 10 ppm	≤ 20 ppm (sum) (of which H_2S ≤ 5 ppm)	≤ 10 ppm	≤ 20 ppm (sum) (of which H_2S ≤ 5 ppm)	≤ 100 ppm_v	≤ 100 ppm_v
H_2S	≤ 9 ppm		≤ 5 ppm		≤ 20 ppm_v	≤ 80 ppm_v
COS	-		-		-	-
$(CH_3)_2S$	-		-		-	-
Dimethyl sulfide	-		-		-	-
H_2	≤ 50 ppm	≤ 0.75% mol	≤ 500 ppm	≤ 0.75% mol	≤ 2% mol	≤ 2% mol
N_2	‡	≤ 2.4% mol	-	≤ 2.4% mol	*	-
Ar	‡	≤ 0.4%	-	≤ 0.4% mol	*	-
CH_4	‡	≤ 1%	-	≤ 1%	*	-
CO	≤ 100 ppm	≤ 750 ppm	0.12% mol	≤ 750 ppm	≤ 2000 ppm_v	≤ 2000 ppm_v
$O_2+N_2+H_2+Ar+CH_4+CO$		≤ 4%	< 2000 ppm	< 40000 ppm	-	-
Amine	≤ 10 ppm	≤ 1 ppm	≤ 10 ppm	≤ 1 ppm	†	†
NH_3	≤ 10 ppm	≤ 3 ppm	≤ 10 ppm	≤ 3 ppm	†	†
HCN	-	≤ 2 ppm	-	≤ 2 ppm	†	†
Formaldehyde	≤ 20 ppm	-	≤ 20 ppm	-	-	-
Acetaldehyde	≤ 20 ppm	-	≤ 20 ppm	-	-	-
Total aldehydes	-	≤ 10 ppm	-	≤ 10 ppm		
C2+ hydrocarbons	-	≤ 0.12% mol	-	≤ 0.12% mol	-	-
Aromatics	-	≤ 0.1 ppm	-	≤ 0.1 ppm	-	-
C_2H_4	-	n/a	-	-	-	-
Total VOC	-	≤ 10 ppm	≤ 10 ppm	≤ 10 ppm	-	-
Total glycol compounds	-	Follow dew point spec.	-	Follow dew point spec.	-	-
Total carboxylic acid and amide compounds	-	≤ 1 ppm	-	≤ 1 ppm	-	-
Tot P contained compounds	-	≤ 1 ppm	-	≤ 1 ppm	-	-
Ethanol	-	≤ 20 ppm	≤ 20 ppm	≤ 20 ppm	-	-
Methanol	-	≤ 620 ppm	≤ 40 ppm	≤ 620 ppm	-	-
Mercury, Hg	≤ 0.03 ppm	-	≤ 0.03 ppm	-	†	†

Several families of chemicals:

- *Hydrocarbons*
- *Oxygenates (ROH; RC(O)H; RC(O)OH)*
- *Amines*
- *S-derivatives*

*Evaluations to perform **at R&D level** or **through Piloting**.*

QUESTIONS ?
PLEASE CONTACT US

REFERENCES

ODORIZATION STANDARDS AND REFERENCE MANUALS

- AGA Odorization Manual
- ISO 13734
- ISO 16922

[ARKEMA GAS ODORANT](#)

[PRODUCT & SERVICE OFFER](#)

LITERATURE:

2013 QUEST Project documentation: odorant injection study

2014 review on CO_2 transportation
GHGT-12
CO_2 Pipeline infrastructure – lessons learnt
10.1016/j.egypro.2014.11.271

2015: Odourisation of CO_2 pipelines in the UK: Historical and current impacts of smell during gas transport
10.1016/j.ijggc.2015.04.010

2022: Failure Investigation Report – Denbury Gulf Coast Pipelines LLC

CCS Guidelines(2008):
http://pdf.wri.org/ccs_guidelines.pdf

Technical and Economic Characteristics of a CO_2 Transmission Pipeline Infrastructure (European commission-2011)

2023: Pipeline Safety Trust
CO_2 Pipeline Safety : summary for policy makers (May 2023)