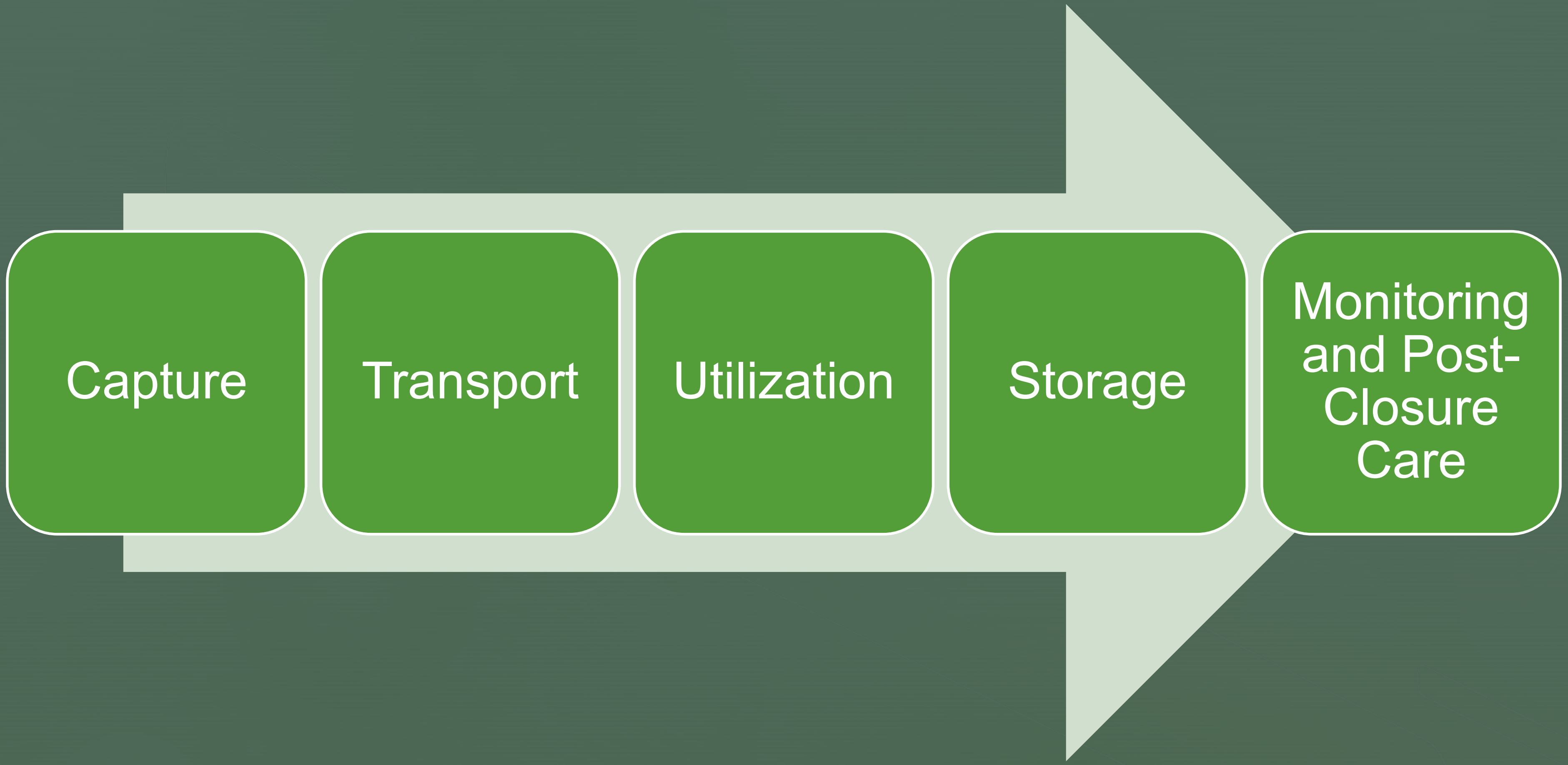
370 CenSARA - CO_2 Sequestration

Amro El Badawy, Ph.D.

March 16 & 17th, 2022

Welcome to Day 2 of 370-CenSARA

Quick Refresher



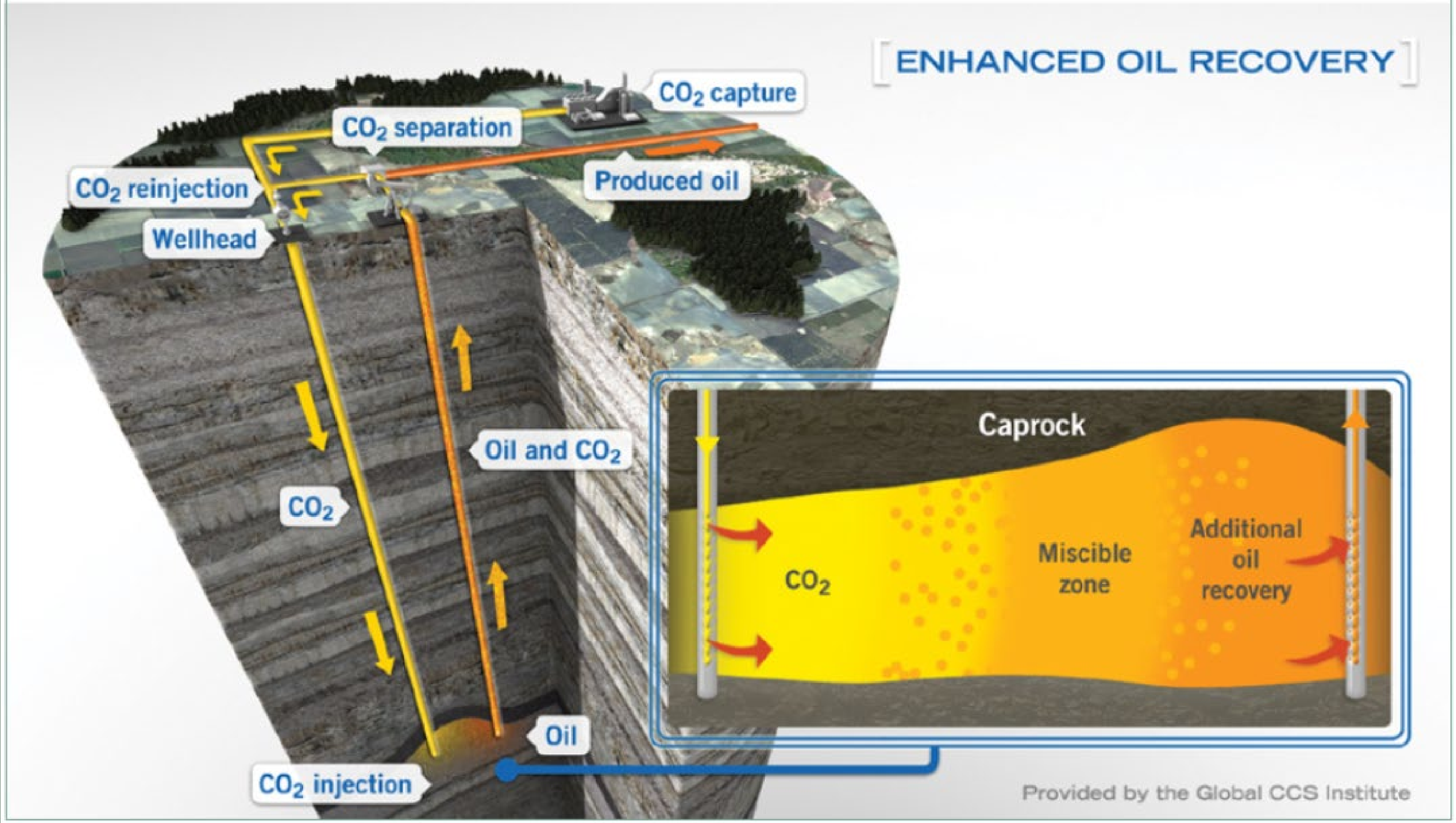
CO_2 Utilization (CCUS)

Utilization

- Options for Industrial Utilization of CO_2?
- What do we need to convert CO_2 to beneficial products?
  - CO_2 conversion Pathways
  - Chemical conversion
    - Thermochemical
    - Electrochemical
    - Photochemical
  - Biological conversion
  - Mineral Carbonation (conversion to sold carbonates)

BEYOND EOR?

Figure 3.2 Enhanced oil recovery



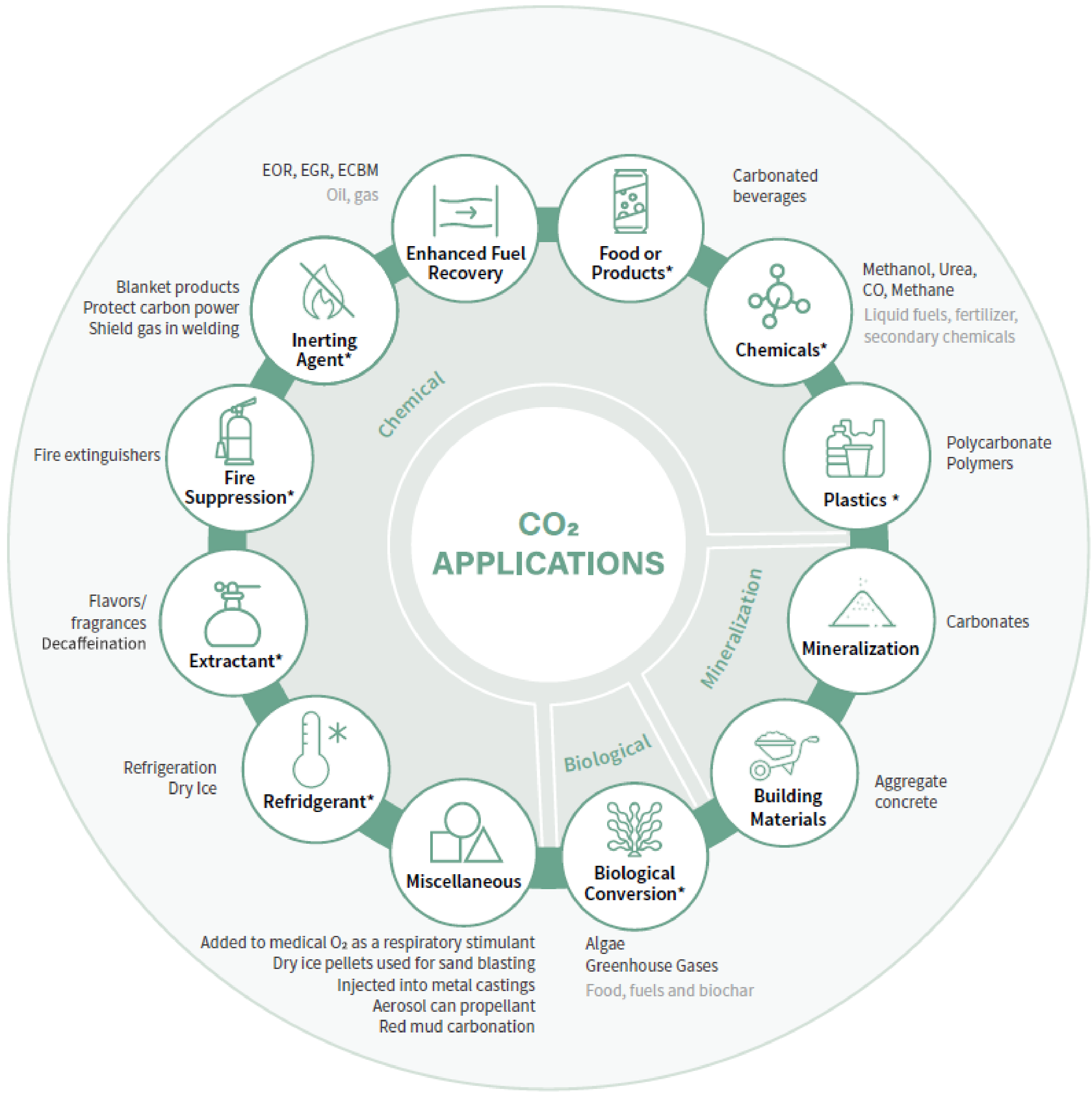
Source: Mai Bui (et.al) 2018

Technology Brief, CARBON CAPTURE, USE AND STORAGE (CCUS), UNECE

Plenty of options!

- Great potential to use CO_2 as feedstock to make a variety of materials through:
    - Chemical Conversion *(produces chemicals and fuels)*
    - Biological Conversion *(produces chemicals, fuels and agriculture products)*
    - Mineralization *(produces construction materials)*

Figure 5.1 CO_2 applications



** Products that use carbon but do not sequestrate carbon permanently*

Source: *Mission Innovation Carbon Capture, Utilization, and Storage Workshop, September 2017*

There is market for it!

- Current CO_2 use is ~120 million tons per year, excluding EOR use
- ~2/3 of the total 120 million tons/year is used for making urea (subsequently produce fertilizers)

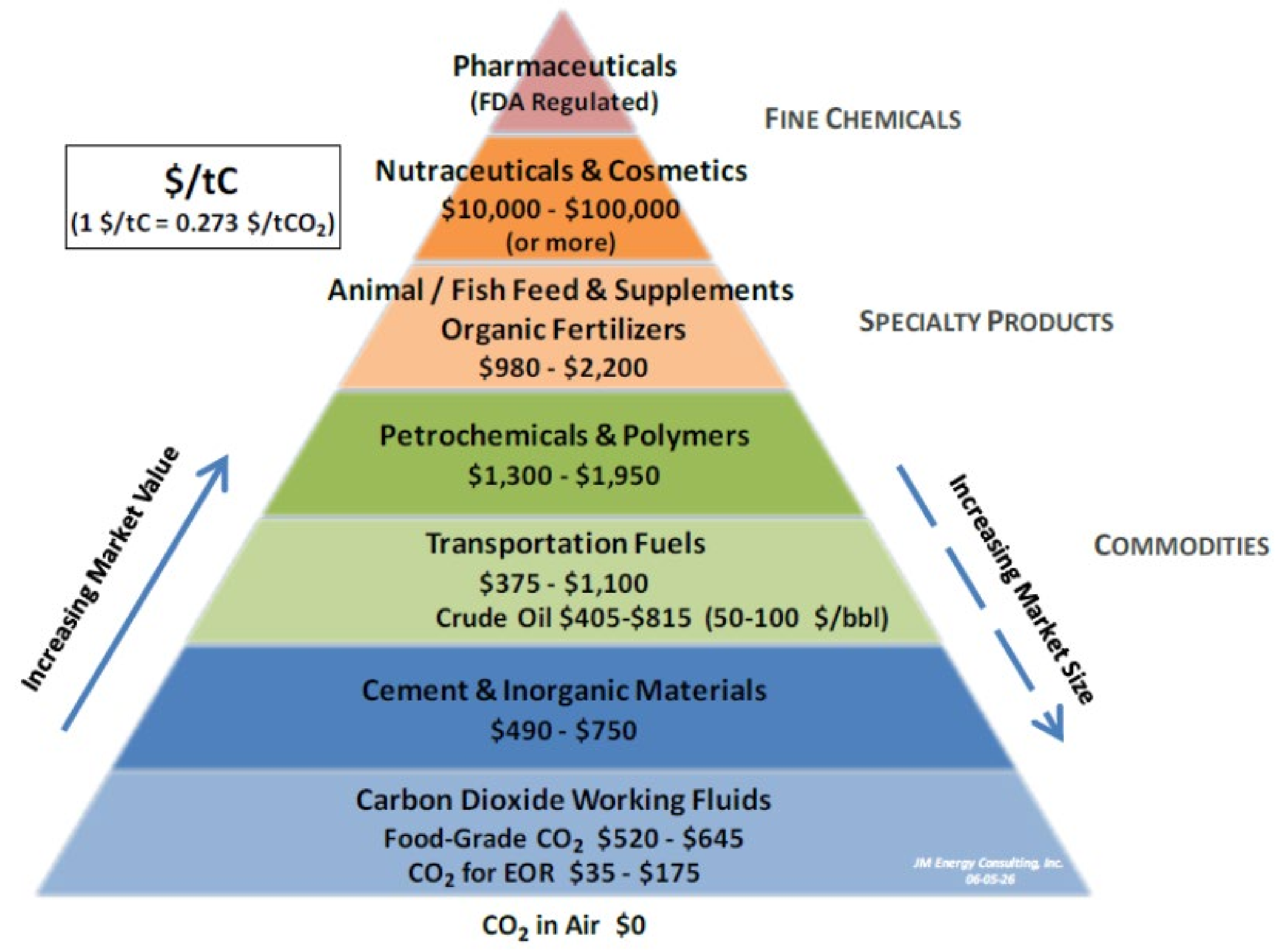
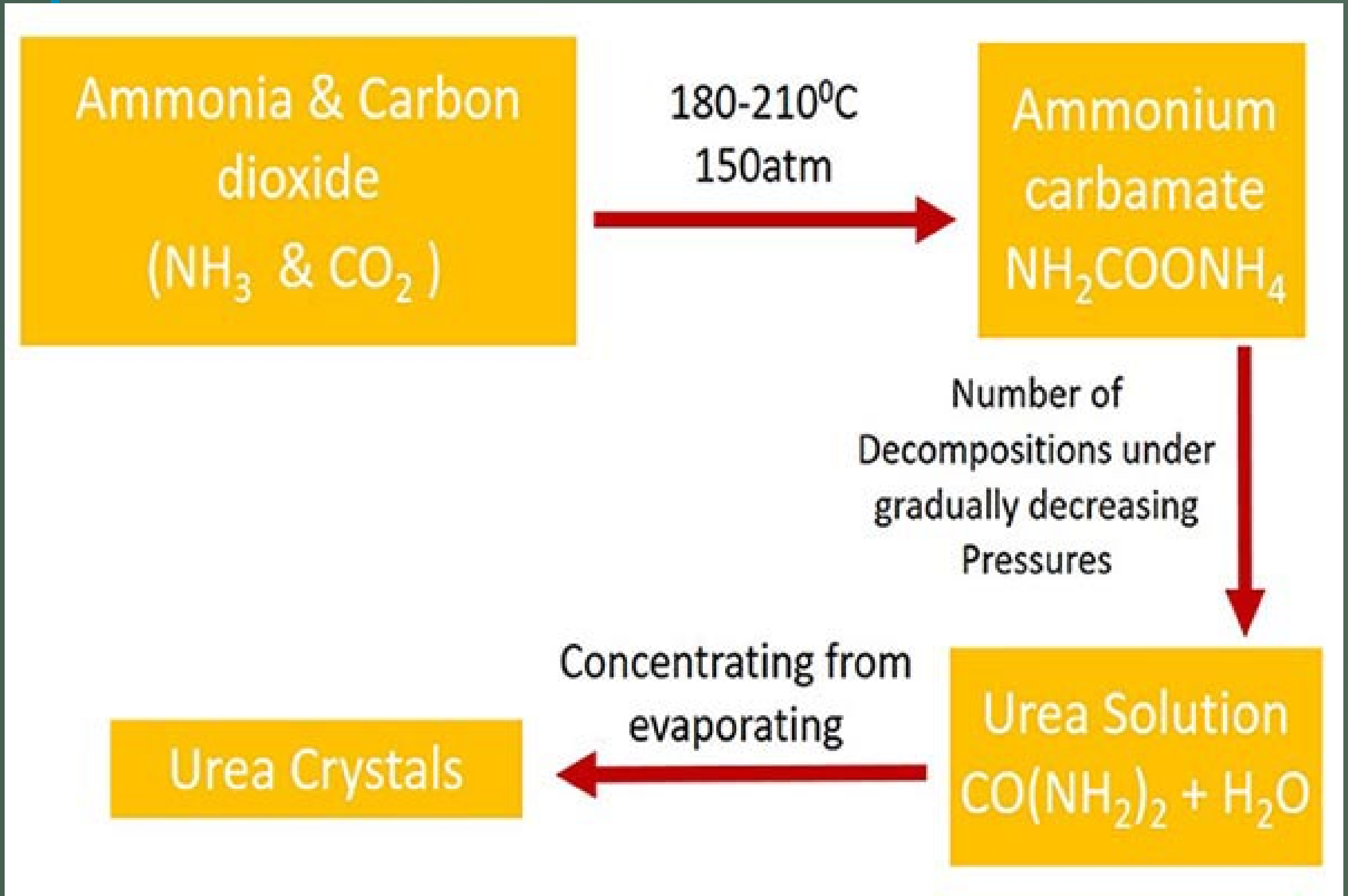
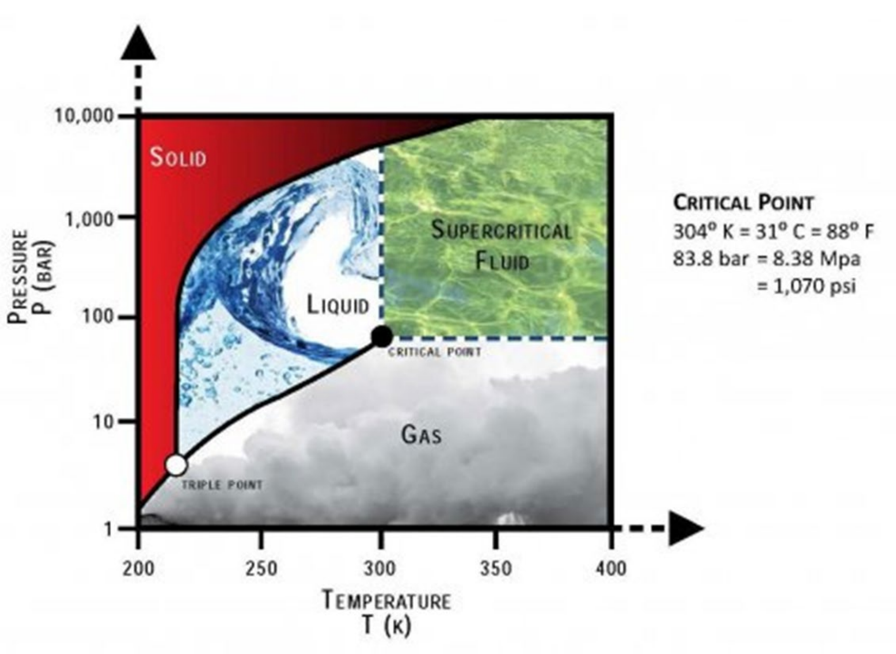


Figure 3. Market value of various carbon-based goods and services

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

If you are interested → here is the process of making urea





200 C = 473 K

150 atm ~ 152 bar

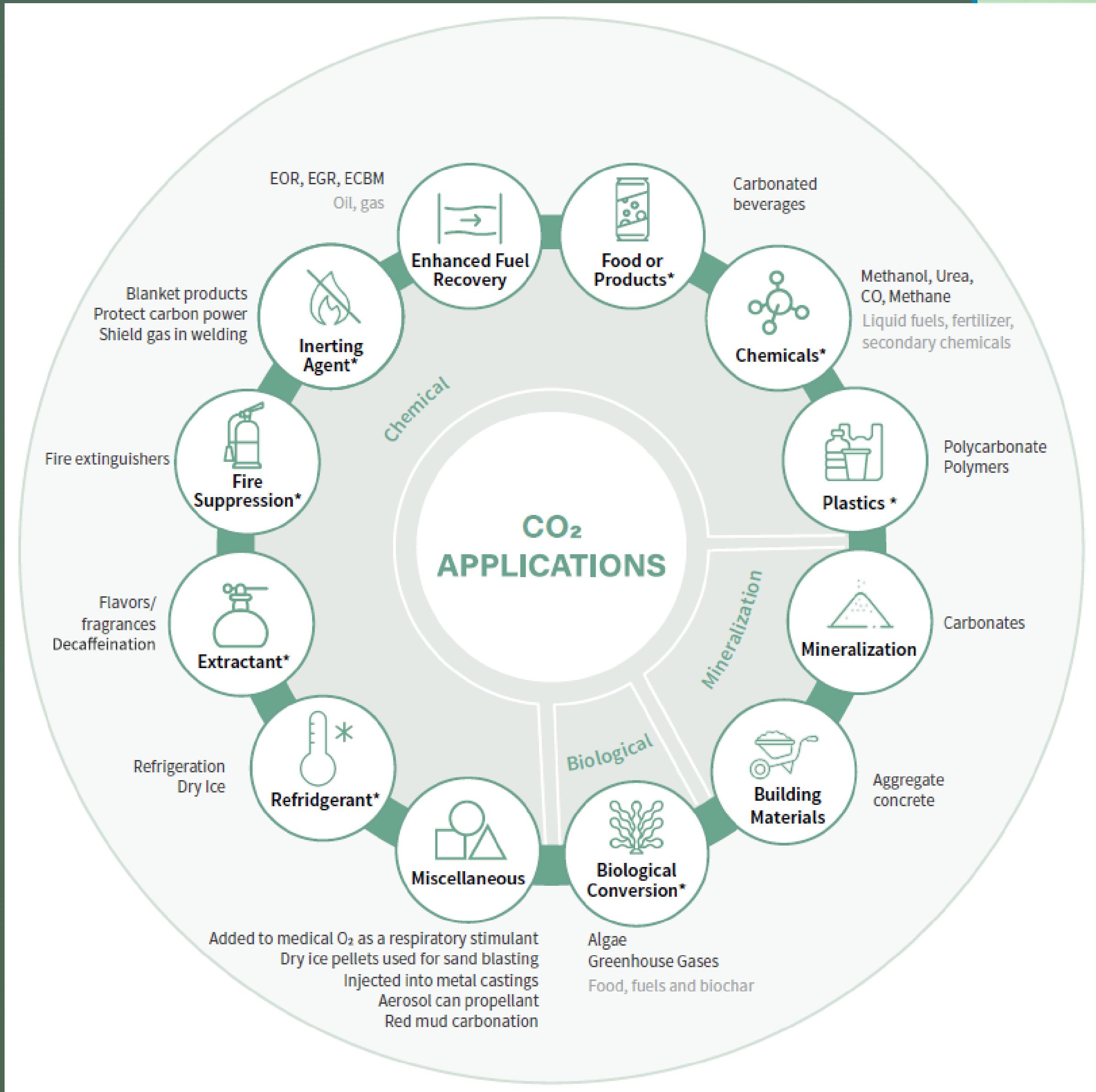
https://www.chemistryscl.com/advancedlevel/industry/urea/main.html

Notes before we dive deeper………

- Not all utilization routes are considered ideal carbon sinks → e.g., converting CO_2 back to liquid fuel → CO_2 will emit again shortly.

- Among the ideal sinks is utilization for making concrete building materials → the CO_2 will be embedded for a long time (permanent sequestration).

- Many carbon utilization routes still require a lot of energy input (especially chemical conversion).
  - If energy input can be generated from renewables (e.g., wind and solar)→ it can reduce the carbon footprint of CO_2 utilization



Technology Brief, CARBON CAPTURE, USE AND STORAGE (CCUS), UNECE

Utilization

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- What would be needed to convert CO_2 to beneficial products?
  - CO_2 conversion Pathways
  - Chemical conversion
    - Thermochemical
    - Electrochemical
    - Photochemical
  - Biological conversion
  - Mineral Carbonation (conversion to sold carbonates)

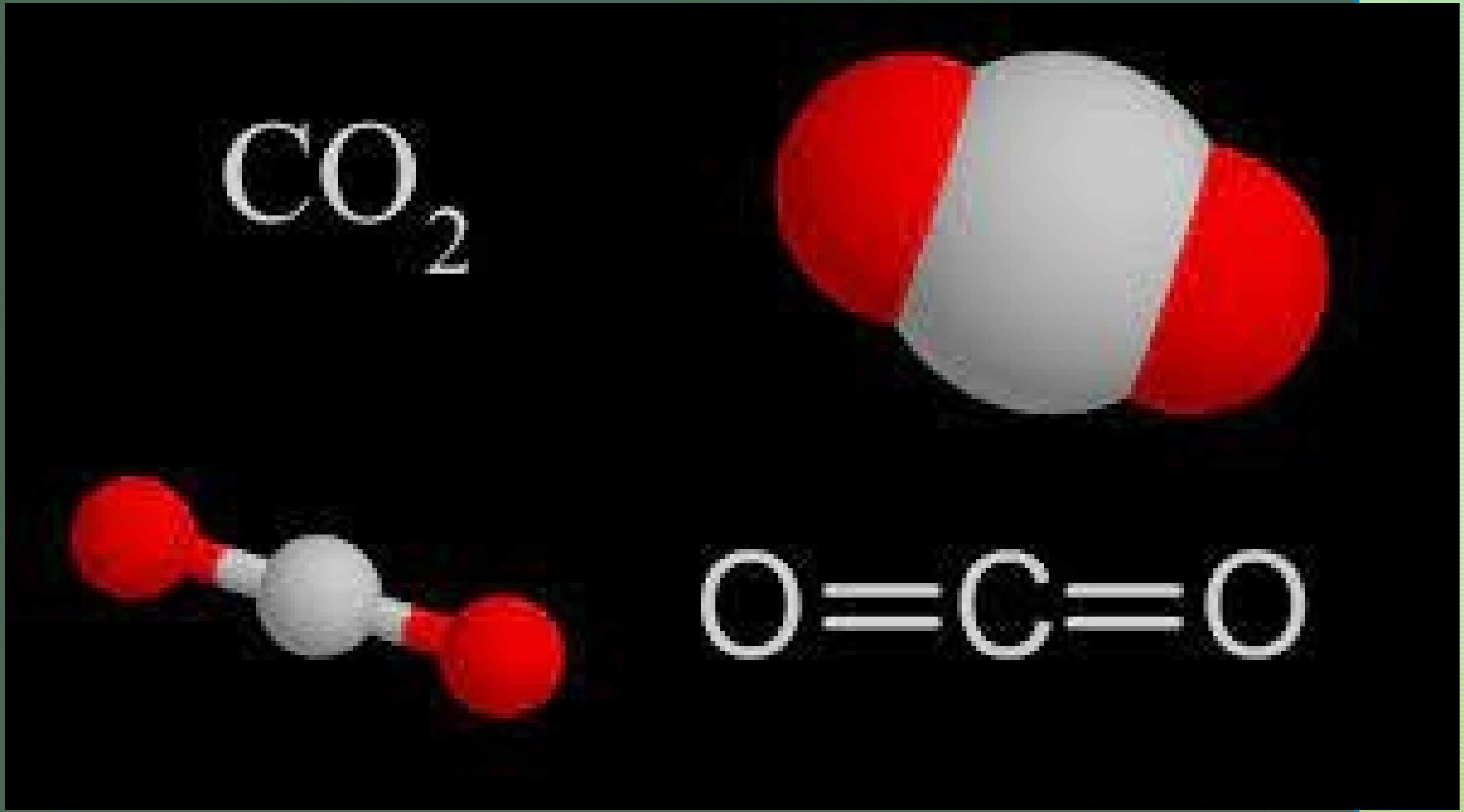
ENERGY is what we need

CO_2 is highly STABLE molecule “i.e., highly inert”

- This means it does not react on its own → “some form of energy is needed to catalyze CO_2 reactions”
- Ok we got that, we know that we need energy →
- The questions is what do we need this energy for?

It is all about the C=O bond

- Need a lot of energy to break that bond.
- When that happens, we have free carbon atoms to use for making so many products.



https://scied.ucar.edu/learning-zone/how-climate-works/carbon-dioxide

Let us get a bit more quantitative

- The figure shows different chemicals we can make from CO_2 molecules as the feedstock
- Each reaction has certain energy requirements *(for example to make aldehydes from CO_2 we need to supply 100 – 300 kJ per mole of aldehyde made)*
- *That's is why it is plus sign (we need to add energy)*
- *In only one case, we do not need to supply energy -→ we actually get energy back → carbonation reaction (mineralization to from solid carbonate) → carbonate has lower energy levels)*
- Red: exothermic reaction (produces energy)
- Blue: endothermic reaction (requires energy)

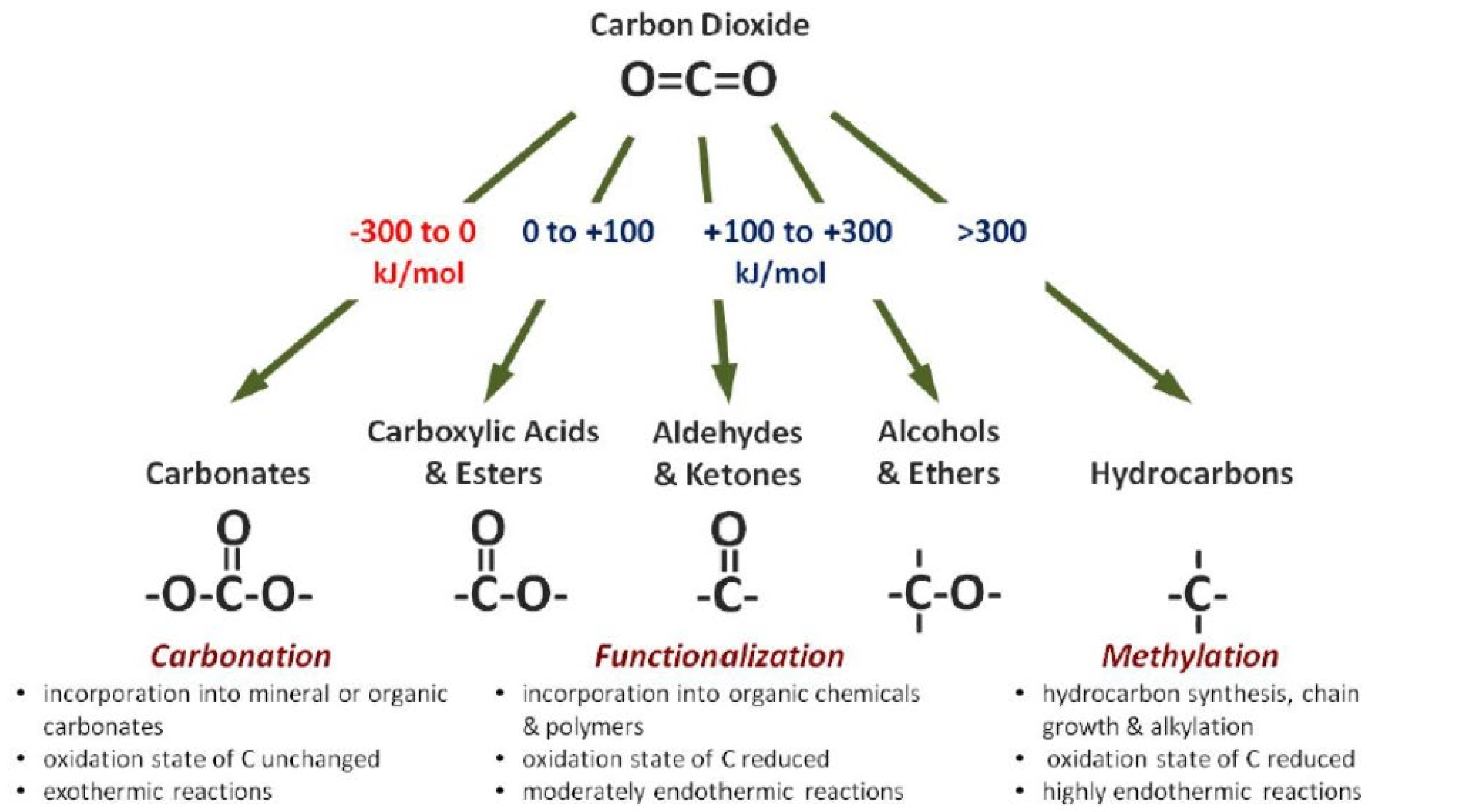


Figure 4. Energetics of CO_2 conversion to various classes of organic and inorganic compounds

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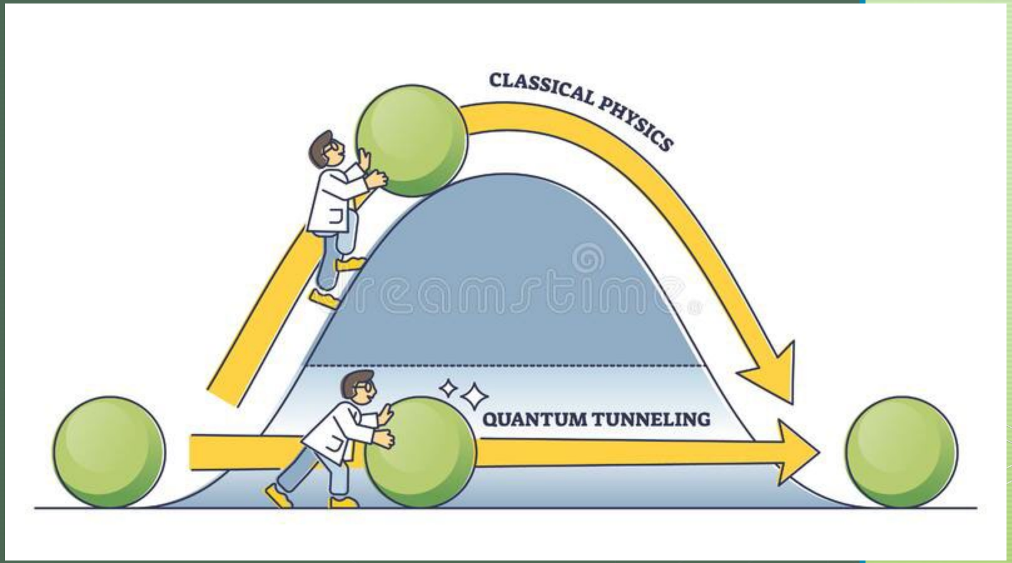
- Ok, we agree that we need to supply energy for utilizing CO_2

How would we supply the energies needed for these reactions to take place?

- Thermochemical (heat)
- Electrochemical (electricity)
- Photochemical (photons)

  - Catalysts are usually used with any of the above sources of energy
  - What does the catalyst do? → reduce energy demand (we still have to supply energy → but lower amounts and we can get the reaction done quicker too)
  - See the image as an analogy of what catalysts do → they make the reactions take other pathways that need less energy



https://www.dreamstime.com/illustration/heisenberg-vector.html

Ok let us discuss the CO_2 chemical conversion pathways with the aid of those energy sources!

Chemical Conversion of CO_2 to make chemicals or fuels

H_2 (from water) + Carbon (from breaking the CO_2 molecules) + energy + catalyst → hydrocarbons

- It is all about breaking the CO_2 molecule and rebuilding new hydrocarbons using the C atoms released from CO_2:
  - Direct pathway (like photosynthesis) → reactants are CO_2 and H_2O → break entirely both molecules & combine C and H to make hydrocarbons
  - Indirect: break only one of the C=O bond (less energy need) → this forms CO as intermediate and will become the building block for making hydrocarbons

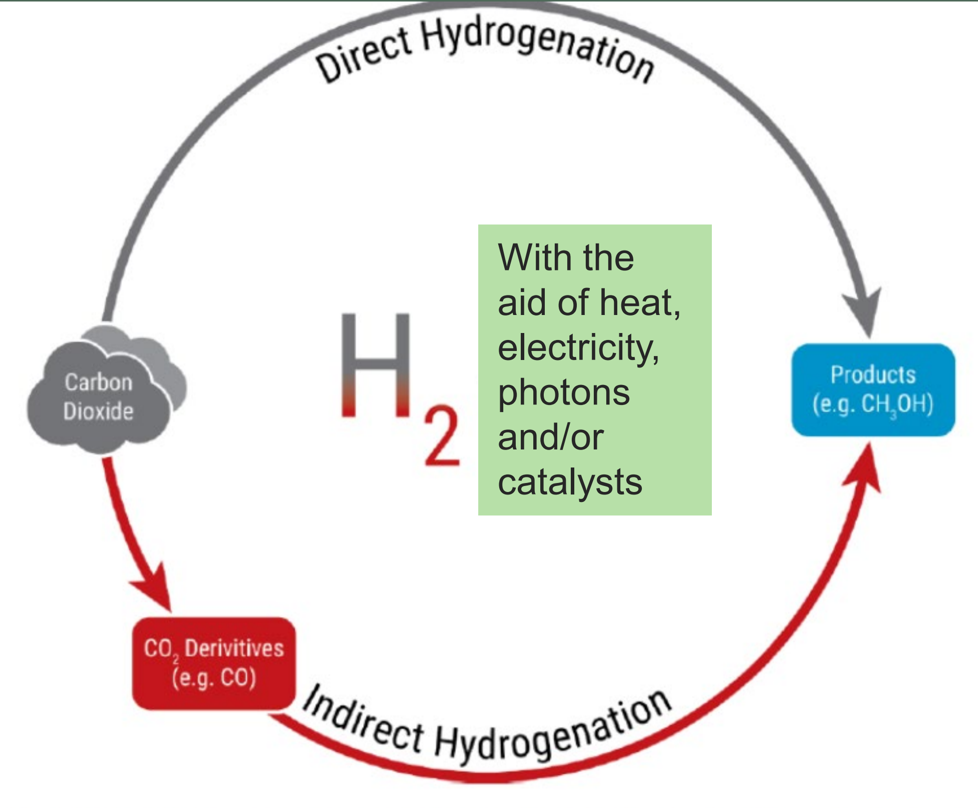


Figure 5. Primary routes for production of fuels and chemicals from

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

To make methanol for example

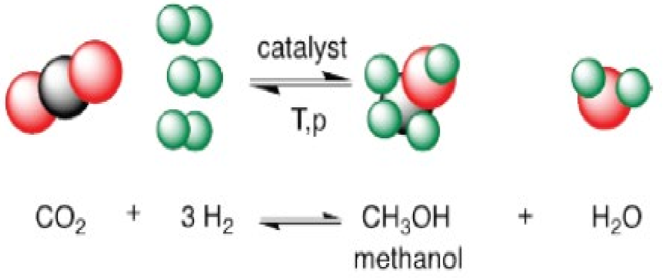
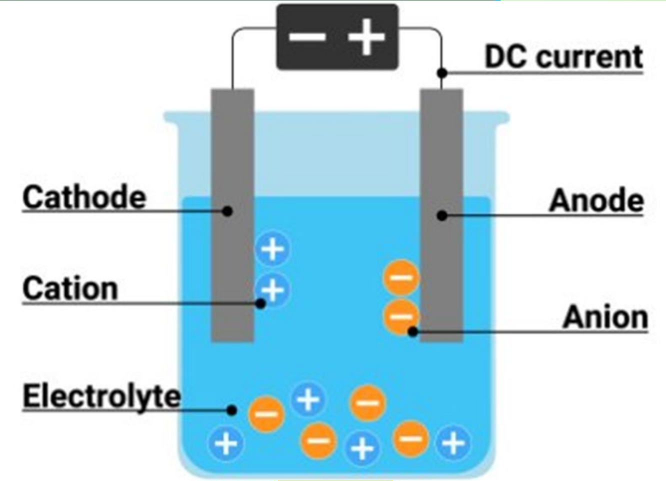
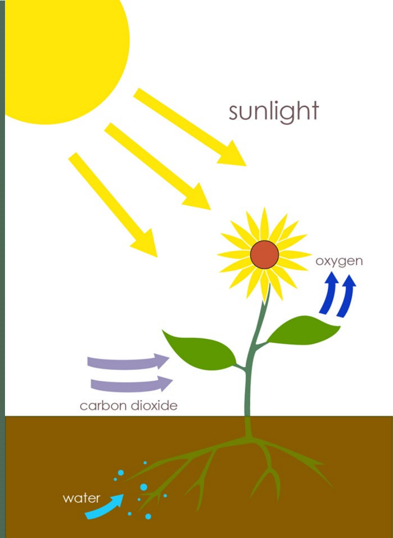


Figure 3.2. Thermochemical conversion of CO_2 to methanol. | Image courtesy of CO2ChemNetwork. Reproduced with permission.

- The forms of energy to supply to the reaction:
  - Thermocatalytic: energy is provided in the form of heat in the presence of a catalyst (e.g., noble metals like palladium and ruthenium)
  - Electrochemical: energy is provided in the form of electricity and the reaction take place in electrochemical cells (catalysts can also be used on the electrodes)
  - Photochemical: solar energy provides the energy needed for the conversion (artificial photosynthesis – learning from plants)
    - In natural photosynthesis –> enzymes act as the catalysts
  - There are hybrid approaches (e.g., combine electrolysis with thermocatalytic)





- Note: methanol is just a first step in the reduction of CO_2 to beneficial products → we can continue further reactions to build higher chain hydrocarbons (remove the oxygen atom and keep building more carbon chains)
- This requires more energy (heat and catalysis) → highly desirable targets are kerosene (C12) and diesel (C18)

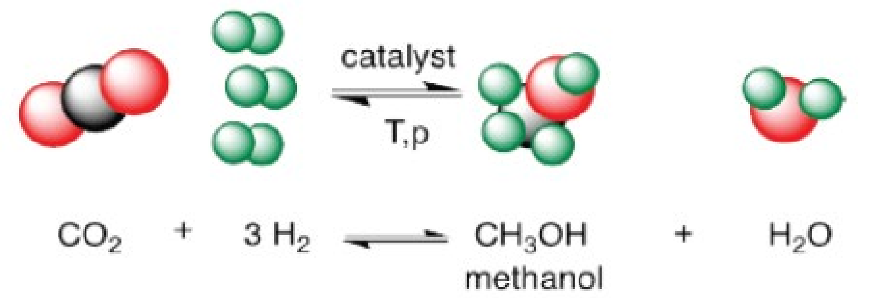
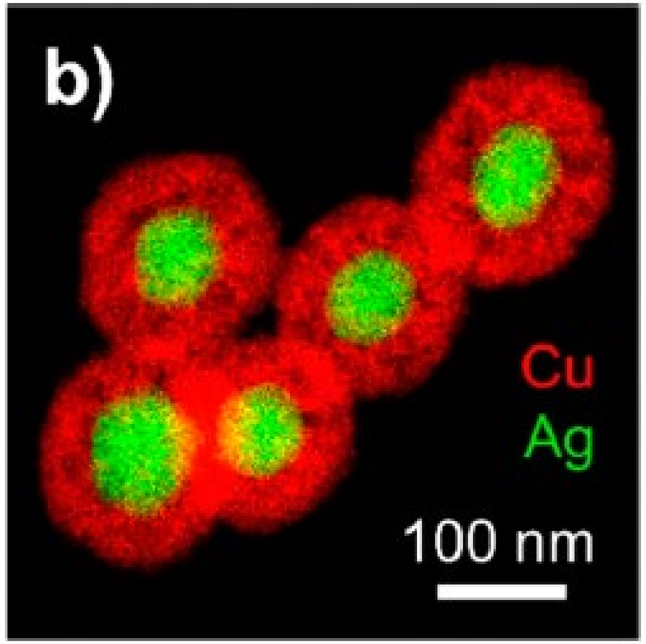
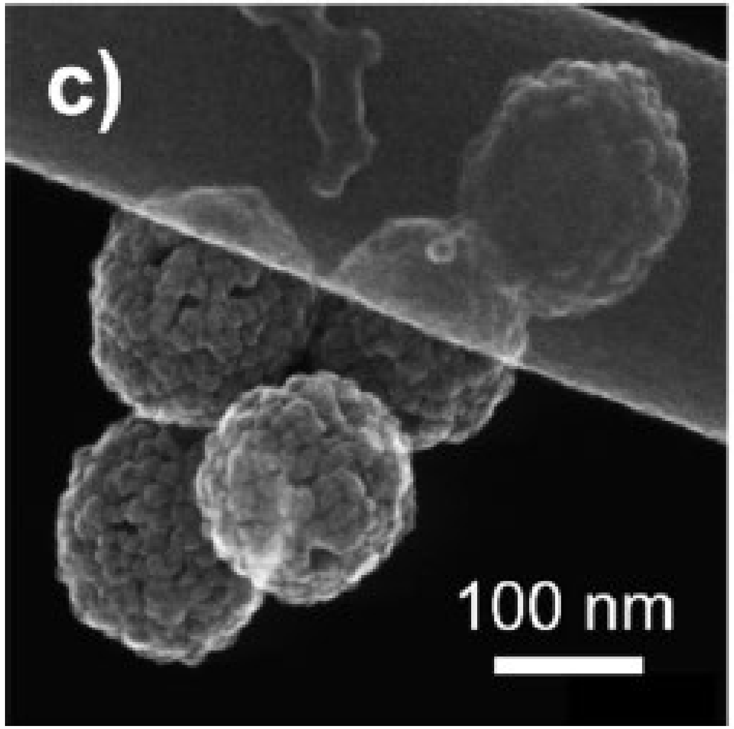
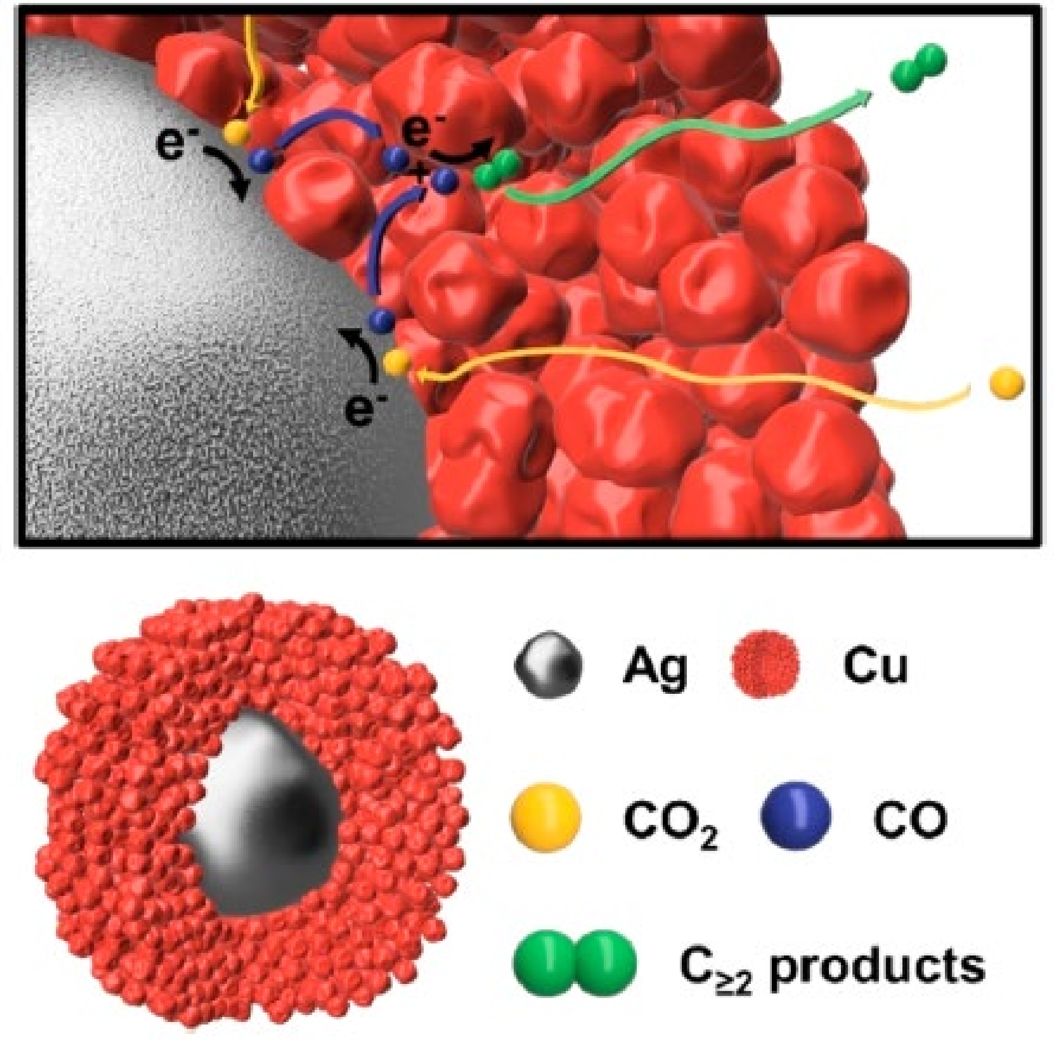


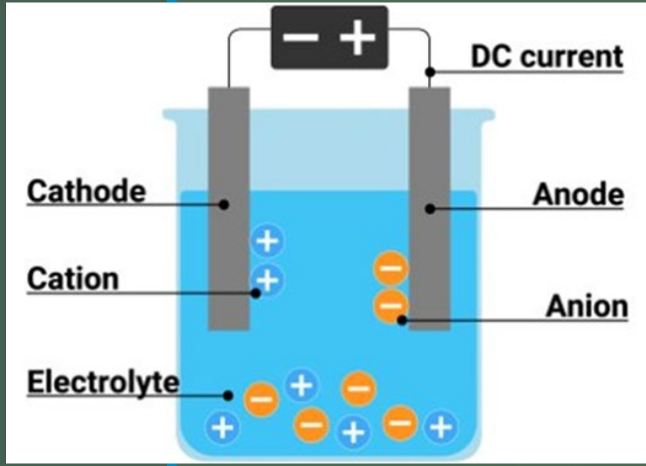
Figure 3.2. Thermochemical conversion of CO_2 to methanol. | Image courtesy of CO2ChemNetwork. Reproduced with permission.

Example: electrocatalytic conversion of CO_2 (indirect conversion route)









O'Mara, Peter B., et al. "Journal of the American Chemical Society 141.36 (2019): 14093-14097.

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Biological Utilization

- Photosynthetic species (e.g. algae) use CO_2 as their carbon source
- What do we get from growing algae?

Biological Utilization

- What do we get from growing algae?
  - Algae could be used for making biofuel
  - Algae can become feed for animals
  - Algae can be grown in wastewater → contribute to treatment and recover nutrients
  - Notes:
    - algae produce a lot of biomass per hectare than terrestrial crops
    - Algae does not need high purity CO_2 (capture may not be needed)

Table 2. Potential microalgae products and prices

Product	Substitutes	Price	Unit[a]
Biodiesel	Diesel	$2.27	USD/gal
Bio-ethanol	Gasoline	$3.96	USD/gal
Bio-methane (fuel)	Liquified petroleum gas	$1.92	USD/gal
Jet fuel (bio-jet)	Jet fuel	$2.49	USD/gal
Electricity	Fossil energy	$0.13–$0.21	USD/kWh
Bio-methane (electricity)	Natural gas	$0.05–$0.06	USD/kWh
Biofertilizers	Synthetic fertilizers	$0.25–$0.63	USD/kg
Biostimulants	Growth promoters	$37.50–$312.50	USD/kg
Biopesticides	Synthetic pesticides	$5.00	USD/acre
Bioplastics	Fossil based plastics	$1.75	USD/kg
Food	Proteins, carbohydrates, oils	$50.00	USD/kg
Beta-carotene	Synthetic/natural	$275.00–$2,750.00	USD/kg
Omega-3 polyunsaturated fatty acids	Fish	$50.00	USD/g
Aquaculture	Fishmeal/fish oil	$68.75–$625.00	USD/kg
Livestock feed	Soybean meal	$300.00	USD/tonne
Feed additives	Botanicals, antibiotics	$20.00	USD/kg

Source: Adapted from https://bioenergykdf.net/billionton2016/overview

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

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Mineral Carbonation

- What is it?
- React CO_2 with minerals to produce solid carbonates
- Carbonates have lower energy state than CO_2 → no energy input for the reaction itself (see Figure)
- Permanent CO_2 sequestration:
  - In-situ, when we inject CO_2 in the ground
  - Ex-situ, when we utilize CO_2
- The raw materials for mineralization of CO_2 are abundant (e.g., silicate rocks and a variety of industrial wastes)

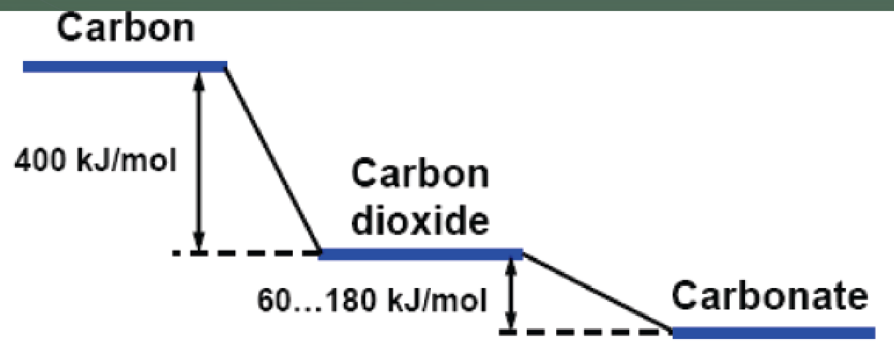


Figure 3.10. Thermodynamics of carbon mineralization.
| Image courtesy of Ah-Hyung Park, Columbia University

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

Here is how the reaction works…..

- Notes:
  - M is a divalent metal like Ca^{2+} and Mg^{2+} and Fe^{2+}
  - The properties of the solid carbonate formed (e.g., magnesium carbonate or calcium carbonate) depend on the feedstock metal oxide (MO) used
  - The CO_2 does not need to be pure (so capture process can be omitted)

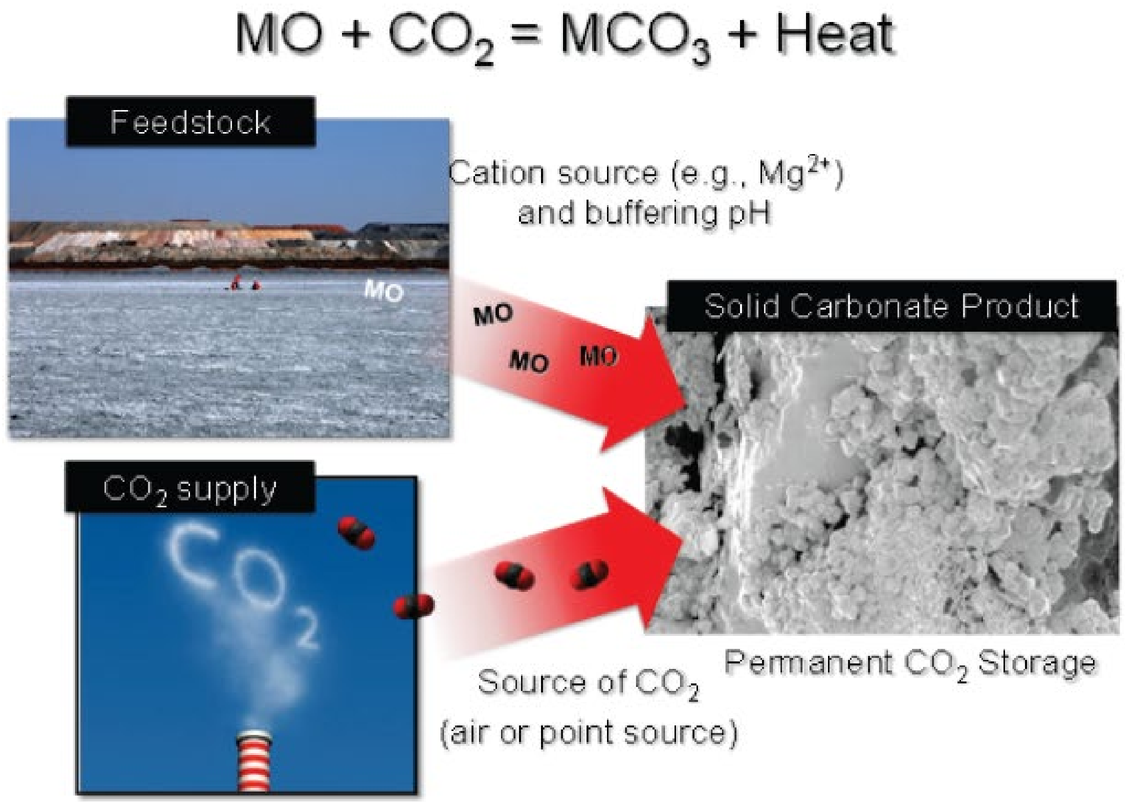


Figure 3.12. Conceptual framework for carbon mineralization. |Image courtesy of Greg Dipple

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

Potential Feedstock for Mineral Carbonation?

- Magnesium rich-ores (e.g., dunite, harzburgite and serpentinite)
- Alkaline mine waste and tailings (generated when mining nickel, chrome, platinum, diamond, copper , gold, and more)
- Alkaline industrial solid residues: example, coal fly ash, waste concrete, cement kiln dust, paper mill water, MSW incineration residues, asbestos waste, steel making byproduct (slag)
- Brines (contain substantial amount of Ca and Mg → thus, it can work
- The key in all the above materials, they have these metal oxides (e.g., CaO and MgO) needed for the reaction

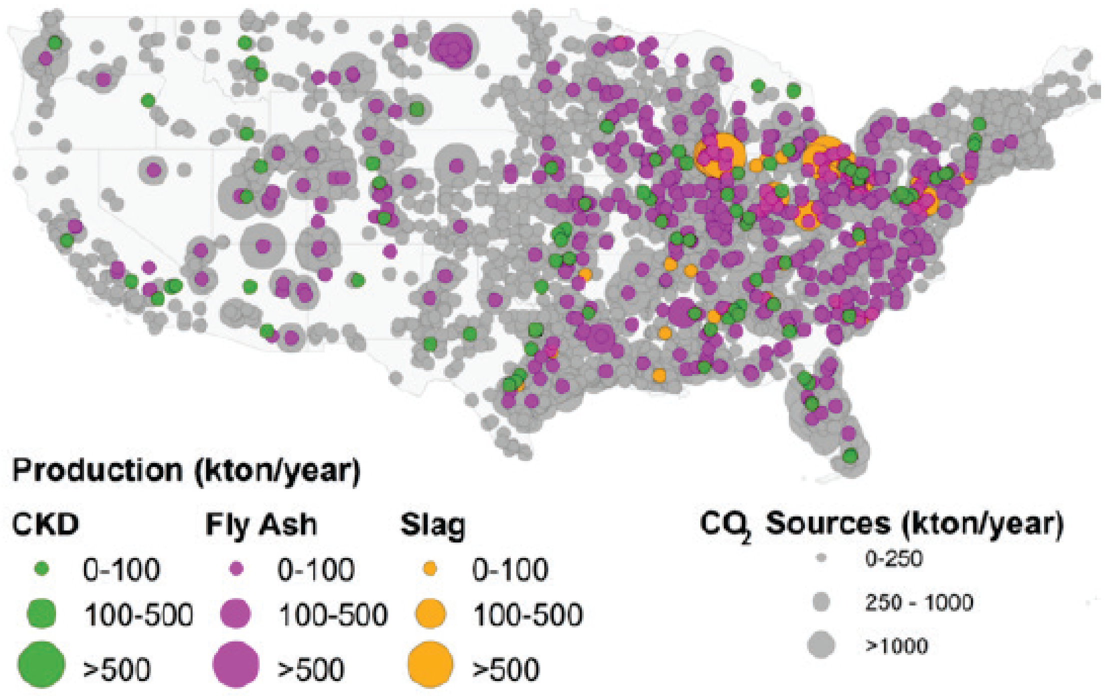


Figure 3.14. Industrial sources of residues (CKD: Cement Kiln Dust and stationary sources of CO_2 in the US). | Reprinted with permission from A. Kirchofer et al. 2013. Environ. Sci. Technol. 47(13), 7548–7554. Copyright 2013 American Chemical Society

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

Examples of Mineral Carbonation Reactions

Olivine:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 89\ kJ\ mol^{-1}CO_2 \quad (2a)$$

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64\ kJ\ mol^{-1}CO_2 \quad (2b)$$

Wollastonite:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 + 90\ kJ\ mol^{-1}CO_2 \quad (2c)$$

IPCC Special Report on Carbon Capture and Storage, 2005

- Yes, carbon mineralization produces heat. But this does not mean that carbon mineralization in industrial processes does not use energy → energy is needed to run the reactors, pump liquids and CO_2 into reactors, etc.

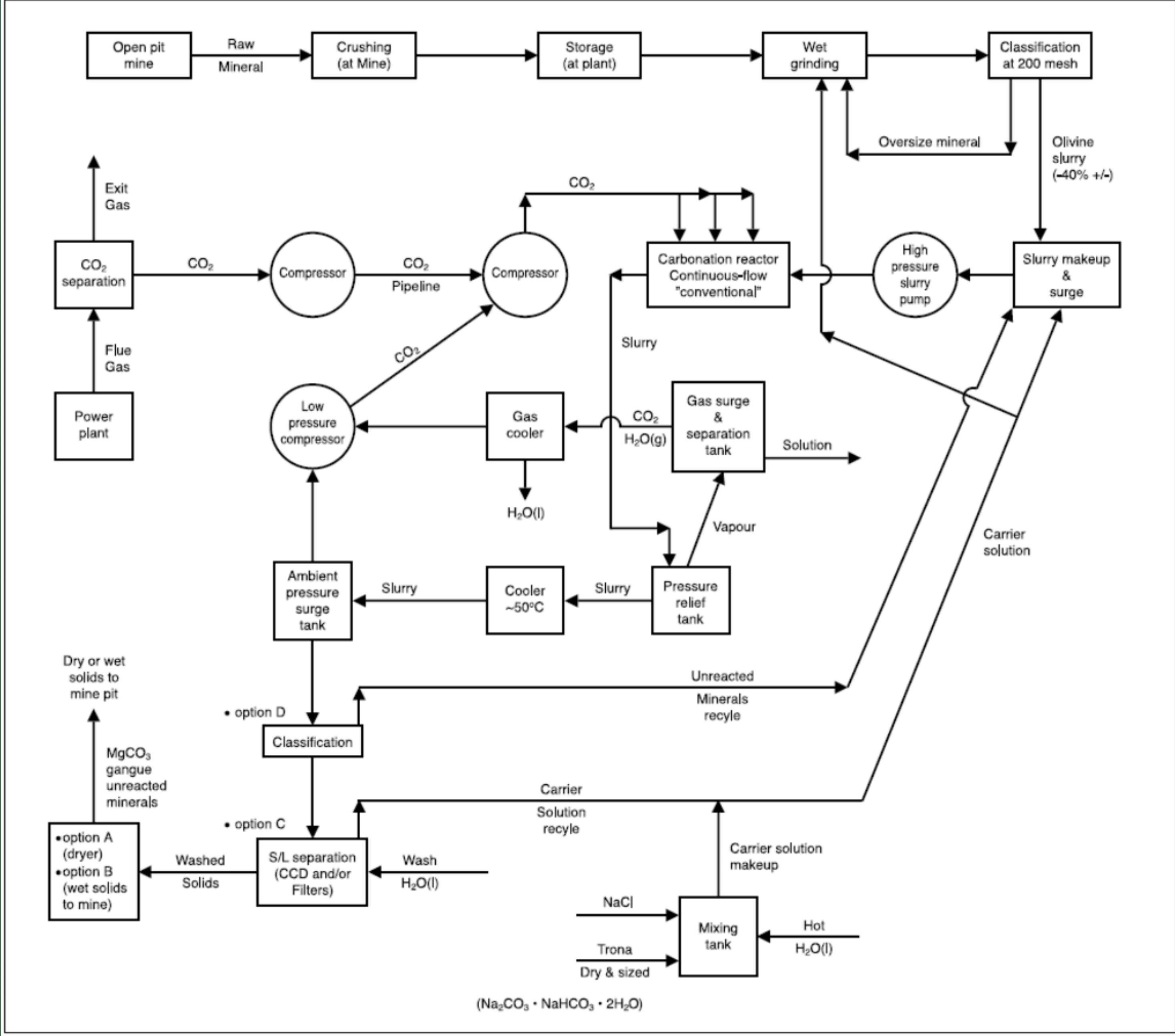


Figure 7.3 Process scheme of the single-step mineral carbonation of olivine in aqueous solution (Courtesy Albany Research Centre) 'Single-step' indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, wherea more steps are of course needed for the whole process, including preparation of the reactants and separation of the products.

IPCC Special Report on Carbon Capture and Storage, 2005

What products we can get from the mineral carbonation?

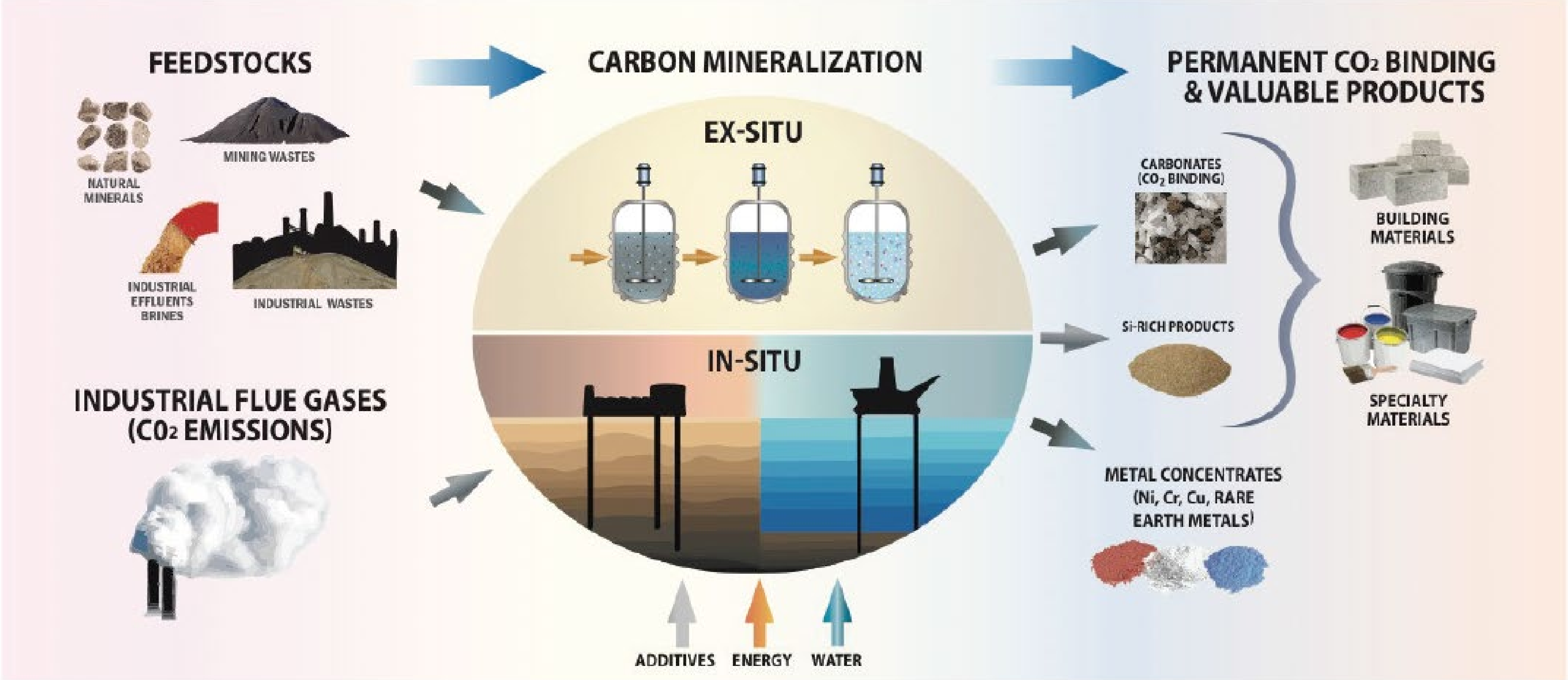
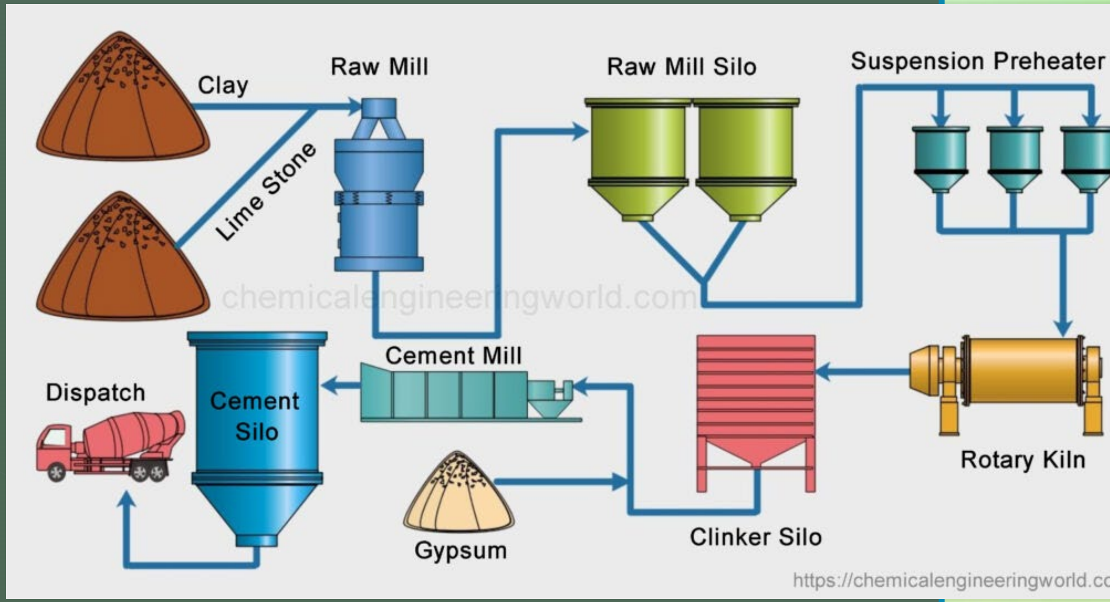


Figure 3.15. Scheme of carbon mineralization and of the range of its products. | Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique; Au-Hung Park and Xiaozhou Sean Zhou, Columbia University

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

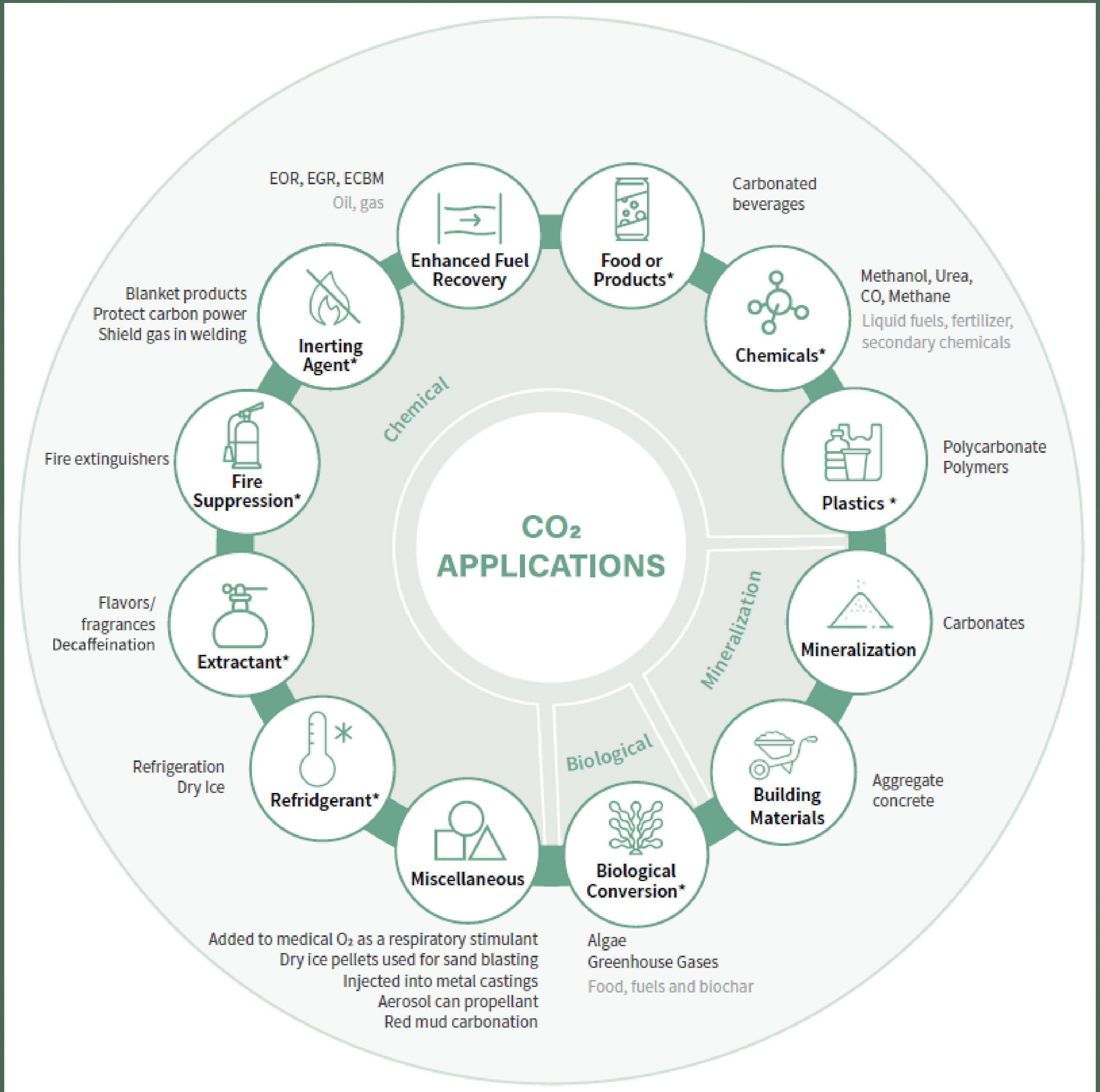
Mineral Carbonation to Produce Construction Materials

- Let us first remember how cement is made → it all starts from limestone ($CaCO_3$)
- Options for CO_2 utilization in construction materials
  - Indirect utilization (make cement with it): perform a mineral carbonation process using any of the feedstock types discussed earlier and CO_2 captured from any source (even from cement manufacturing process) → $CaCO_3$ is generated → that is the raw material used in making cement
  - Direct utilization (cure concrete with it): CO_2 is added to concrete during curing -→ carbon mineralization reactions happen inside the concrete ($CaO + CO_2$) → the mineralized CO_2 incorporated inside the concrete mix improves the strength of the mix and even less cement can be used in making the concrete (sequestered permanently)



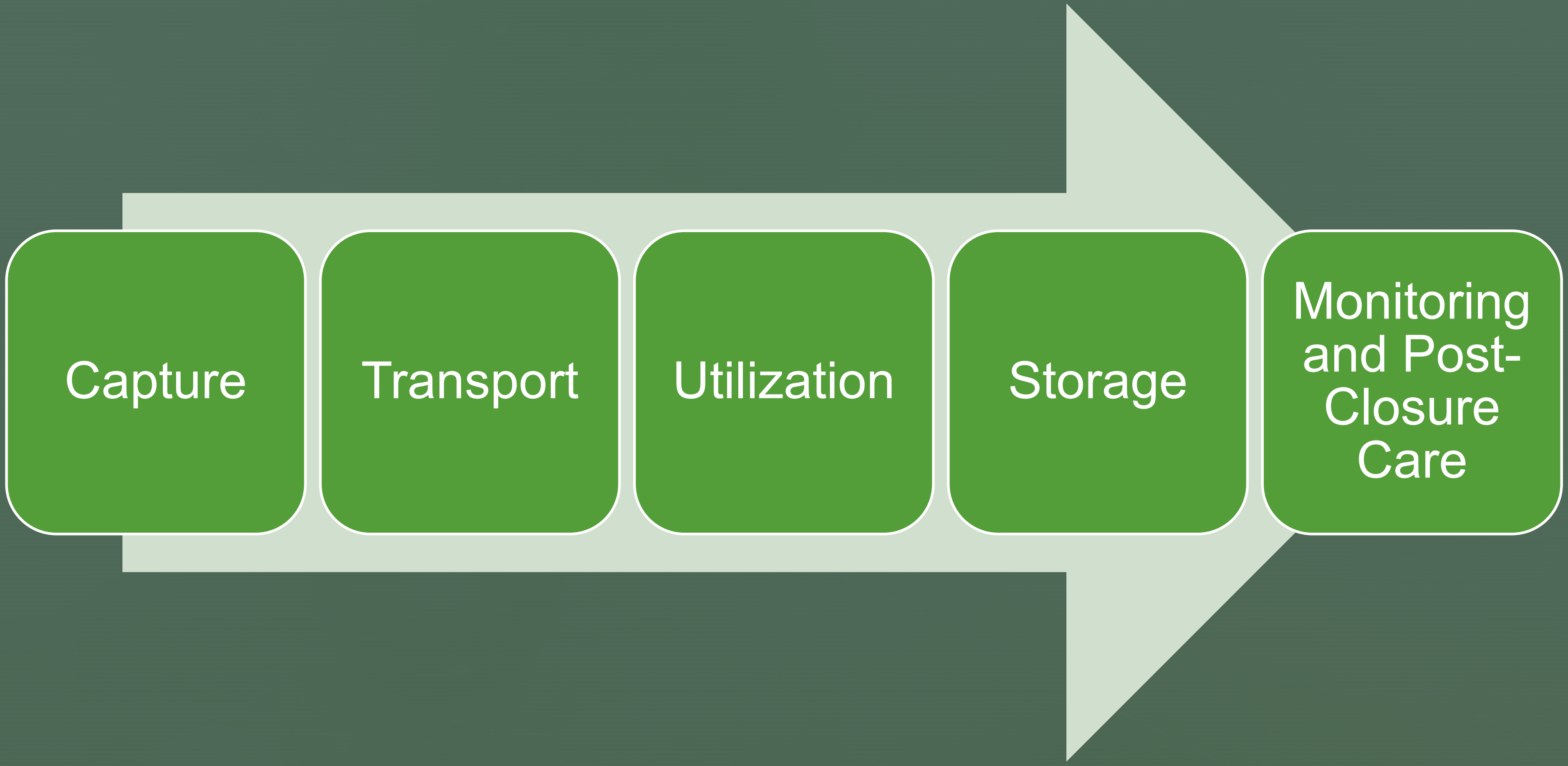
Concluding remarks

- There are various opportunities for utilization of CO_2!
- Each conversion process will need different system and equipment (thinking from an air quality compliance standpoint)
- But all processes will need an energy source → emissions are expected → so these sources would follow the regular air quality standards/requirements

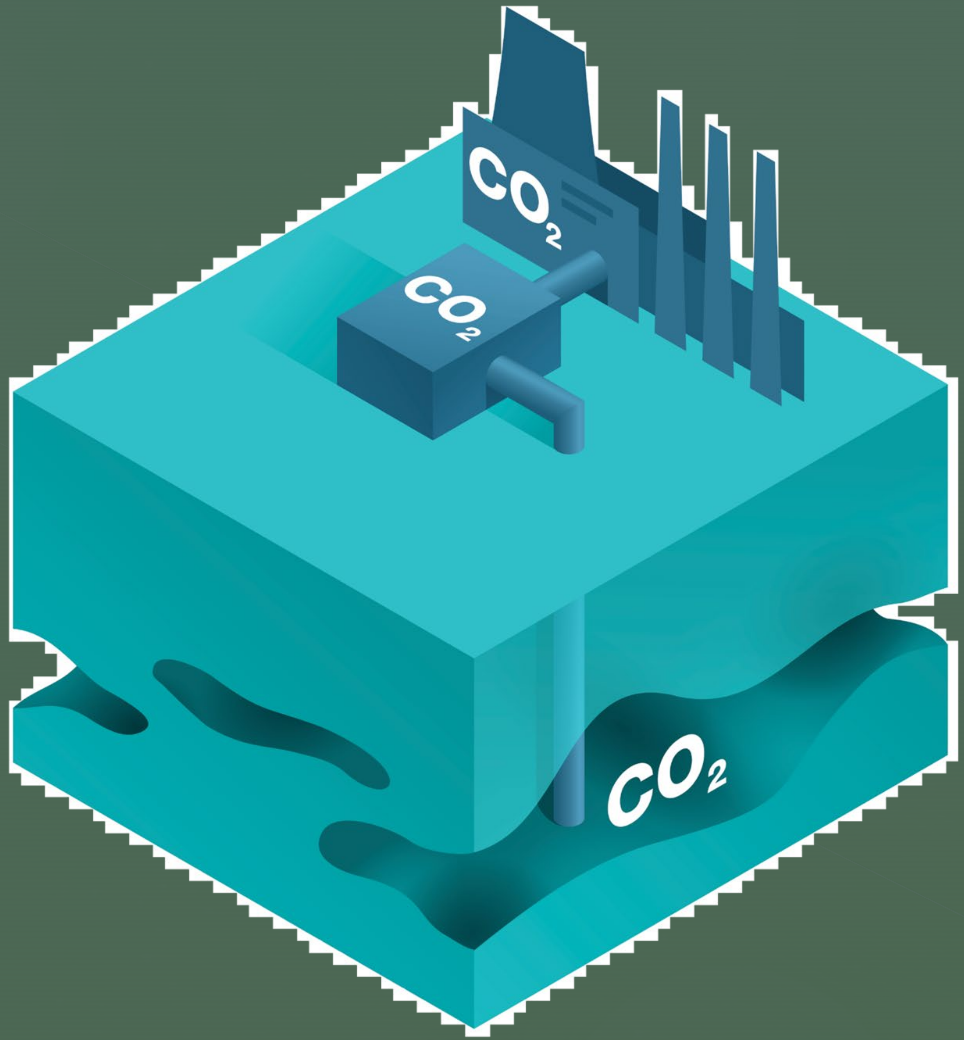


Technology Brief, CARBON CAPTURE, USE AND STORAGE (CCUS), UNECE

That was it for the components of the CCUS!



Risks & Impacts of CCS Projects



https://www.deepcstore.com/other-ccs-projects

CO_2 Leakage is the main concern

- But why we need to worry → CO_2 is not a criteria pollutant (☺)

CO_2 Leakage → Endangers USDW (among others)

(that is the main philosophy behind Class VI well regulations)

- CO_2 leaked + H_2O → carbonic ACID
  - Corrosive and can mobilize metals and toxics in the water
- Also if brine leaks from the storage formations → it will degrade the quality of the USDW (e.g., increases salinity)
  - expensive treatment system would be need it to make it drinkable again (RO might be the only options)

https://www.westech-inc.com/products/reverse-osmosis-system

Who/What will be impacted by the leakage of the stored CO_2? (i.e., receptors)?

- Atmosphere
- People
- Habitats
- Agriculture land
- Lakes an rivers
- Vadose zone Groundwater
- Deep subsurface microbes
- Tectonic plates movement

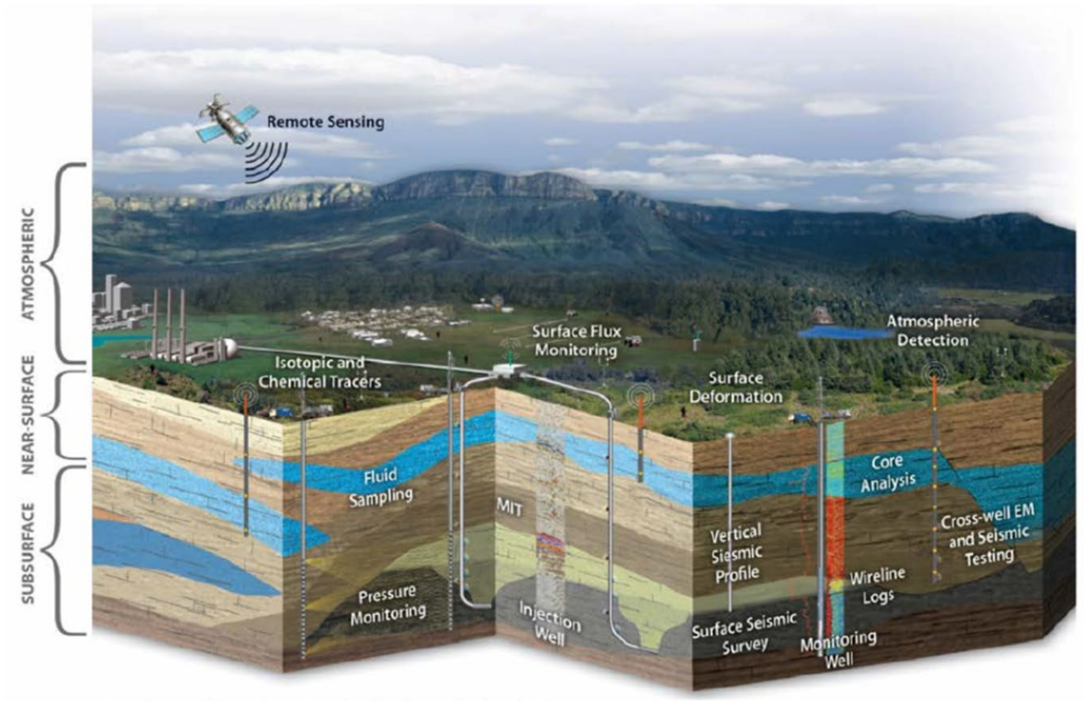


Figure 5-1: Examples of Various Field Monitoring Techniques

Backround Image Courtesy of Schlumberger Carbon Services

Let us now talk about some of the potential impacts on those receptors

Receptor of Leaked CO_2	Potential Impacts
Atmosphere (itself)	??????

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007

Receptor of Leaked CO_2	Potential Impacts
Atmosphere (itself)	Increase GHG impacts
Agriculture land	?????

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007

Receptor of Leaked CO_2	Potential Impacts
Atmosphere (itself)	Increase GHG impacts
Agriculture land	1) Elevated CO_2 in soil can harm plant growth (soil can turn **anaerobic** and this will impact soil microbes) 2) Phytotoxic effects on plants when CO_2 > 5% 3) If moisture in soil is high -→ leaked CO_2 will make the water acidic → Impact plans and soil microbes
Vadose zone	?????

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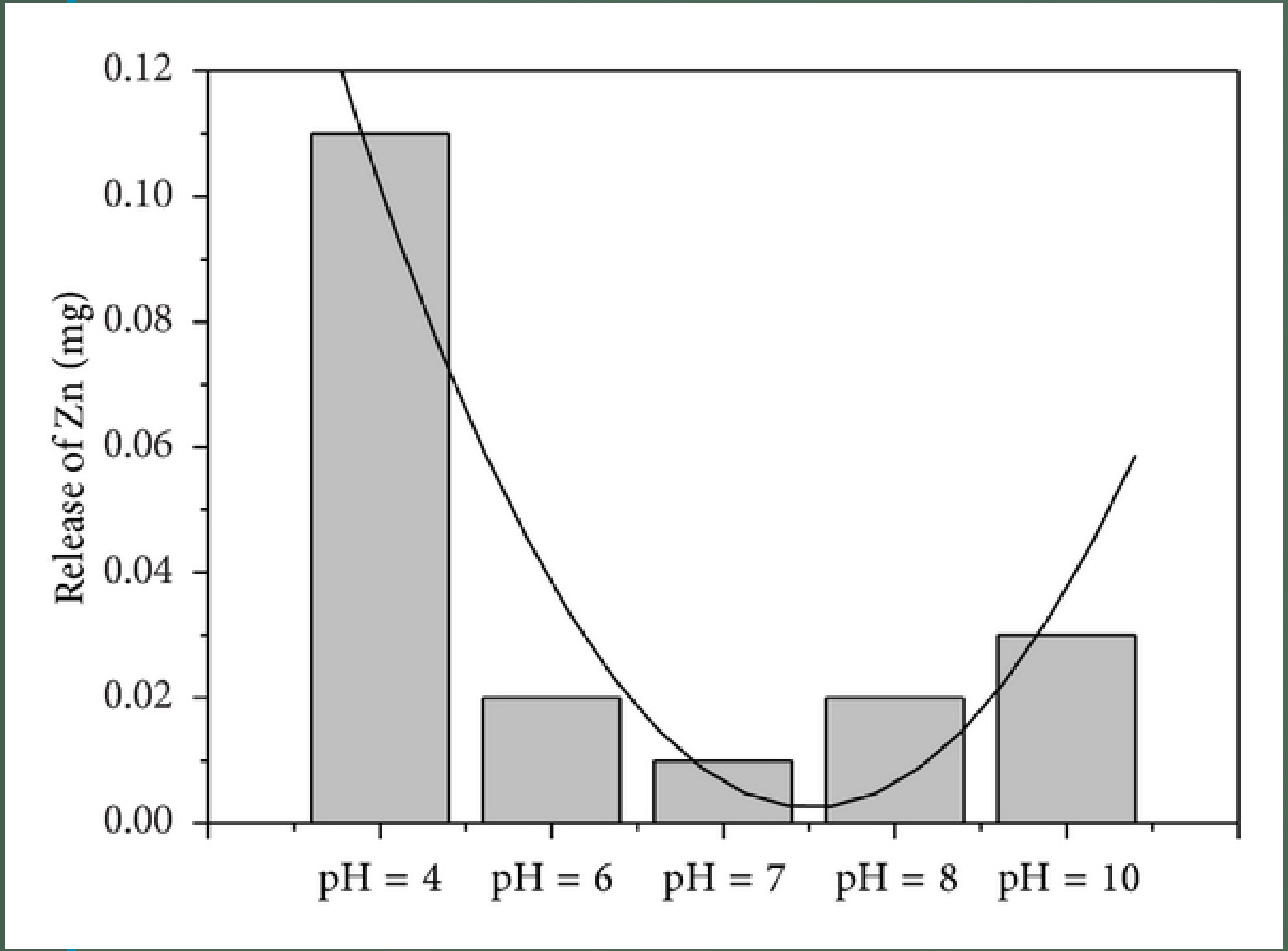
Vadose Zone	CO_2 would be in contact with drinking water sources → acidic conditions → potential release (mobilization) of contaminants depending on the composition of soil

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007



https://www.hindawi.com/journals/jchem/2013/434012/

- Metals are more soluble in acidic pH conditions

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Vadose Zone	CO_2 would be in contact with drinking water sources → acidic conditions → potential release of contaminants depending on the composition of soil
Lakes and rivers	CO_2 leaked into bottom of lakes would be problematic in seasons with low mixing conditions → CO_2 will build up at the bottom → anaerobic environments occur -→ less oxygen will be fatal to living species in the lake Water acidification is a problem that can happen in both rivers and lakes because of CO_2 leaks
Deep subsurface microbes	?????????????????????????

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007

Receptor of Leaked CO_2	Potential Impacts
Atmosphere (itself)	Increase GHG impacts
Agriculture land	1) Elevated CO_2 in soil can harm plant growth (soil can turn **anaerobic** and this will impact soil microbes) 2) Phytotoxic effects on plants when $CO_2 > 5\%$ 3) If moisture in soil is high -→ leaked CO_2 will make the water acidic → Impact plans and soil microbes
Vadose Zone	CO_2 would be in contact with drinking water sources → acidic conditions → potential release of contaminants depending on the composition of soil
Lakes and rivers	CO_2 leaked into bottom of lakes would be problematic in seasons with low mixing conditions → CO_2 will build up at the bottom → anaerobic environments occur -→ less oxygen will be fatal to living species in the lake Water acidification is a problem that can happen in both rivers and lakes because of CO_2 leaks
Deep subsurface microbes	Poor knowledge about impacts of CO_2 on microbes in deep formations
Populated areas	???

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007

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Deep subsurface microbes	Poor knowledge about impacts of CO_2 on microbes in deep formations
Populated areas	Leaked CO_2 can pool close to the ground during periods of low wind at concentrations potentially toxic to life (human, animals, and plants) depending on concentrations (see next slide)

Source: adapted from Environmental Assessment for CO_2 Capture and Storage, IEA Greenhouse Gas R&D Programme, Technical Study, 2007

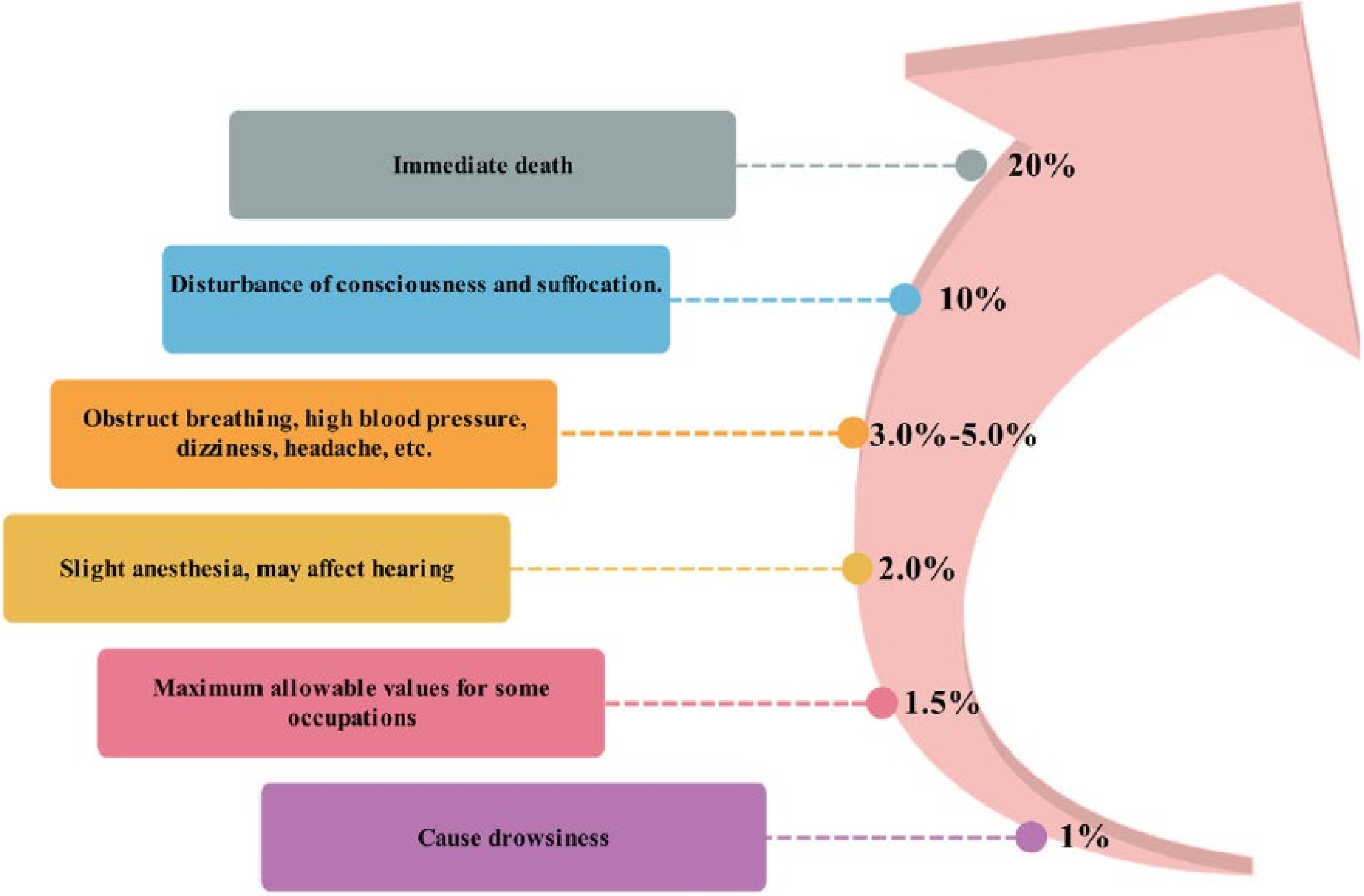


Fig. 9. The harm of different CO_2 concentrations to human health (Witkowski et al., 2013).

Lu, H., Ma, X., Huang, K., Fu, L., & Azimi, M. (2020). Carbon dioxide transport via pipelines: A systematic review. *Journal of Cleaner Production*, *266*, 121994

Other receptors…..

Induced seismicity (impact on earth?)

- Injecting high volumes of pressurized CO_2 (specially when Gigatons-scale are realized) can induce earthquakes
  - Pressures in the subsurface would increase → the effective stresses on geological faults would increase → slips on faults would take place → earthquakes happens
  - Example: several cm of slip on a 1-4 km long fault can cause magnitude 4.0 earthquake

Examples of seismic activity data from CO_2 injection projects

Table 4.1. Summary of seismicity observations at CO_2 injection sites. | Modified from White and Foxall 2016

Site	Type	Operation	Monitoring	Observations
Aneth (USA)	CO_2 EOR		Borehole microseismic	Magnitudes: M1.2 to M0.8 Frequency: 3800 events over 1 yea. Two fault-like clusters
Cogdell (USA)	CO_2 EOR		Regional network	One M4.4 event and 18 M3+ events over a 6 year period. No major seismicity at nearby, similar operations
Weyburn (Canada)	CO_2 EOR	2000 ~ 3 Mtpa	Borehole microseismic	Magnitudes: M3 to M1. Frequency: 100 events over 7 years Diffuse locations
Decatur (USA)	CO_2 disposal	2011–2014 1 Mtpa	Borehole microseismic and surface array	Magnitudes: M2 to M1 Frequency: 10,123 events over 1.8 years Multiple fault-like clusters
In Salah (Algeria)	CO_2 disposal	2004 ~ 1 Mtpa	Shallow borehole microseismic	Magnitudes: M to M1.7 Frequency: 10,000 events over 1 year Indications of fracture stimulation
QUEST (Canada)	CO_2 disposal	2015 ~ 1 Mtpa	Borehole microseismic array	<100 microseismic events from a localized source region in the basement

Accelerating breakthough innovation in carbon capure, utilization, and storage, 2017, DOE

Let us discuss a few things about CCS project risks

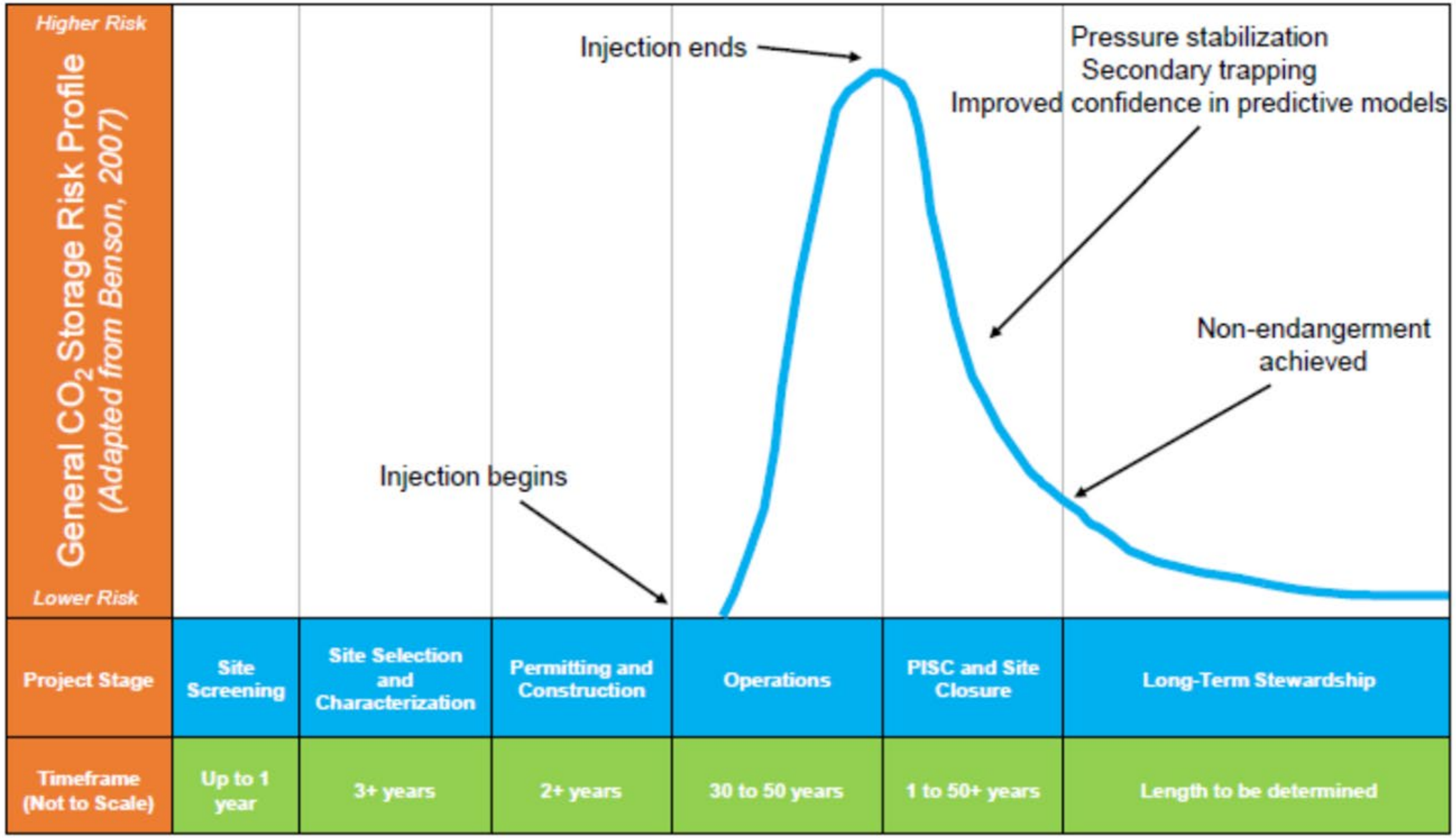
Risk (i.e., probability of occurrence of these events/impacts)

Note 1: Leakage can be gradual or abrupt

- The risks and severity of the impacts on receptors will depend on that
- Gradual release through:
  - Faults or cracks in the well components (for both active and abandoned wells)
- Abrupt (catastrophic):
  - Well blowout (too much pressure and low permeability)

Note 2: the levels of CCS projects related risks change over the lifespan of the project

Exhibit 2-9. Example of a general risk profile over the lifespan of a theoretical CO_2 storage project



Note: Adapted from concepts from Benson (2007), Bromhal et al. (2014), and Pawar et al. (2015) [69, 84, 83]

Since we mentioned “Risk” → Let us chat a little bit about “Risk Assessment”

- Each CCS/Project is different
- Thus → potential risks are different
- As a result → Risk Assessment is performed to qualitatively or quantitatively describe those risks

Risk Assessment Tools/Frameworks

- The DOE's Regional Carbon Sequestration Partnerships (RCSP) used three types of risk assessment to determine the probability and impact of the tasks associated with their CCS projects:
  - Qualitative Risk Assessment – develop non-numeric estimates of risks (e.g., high, medium, low)
  - Quantitative Risk Assessment – develop numeric probabilities of risks
  - Semi-Quantitative Risk Assessment – combination of expert opinion and numeric evidence

BEST PRACTICES: Risk Management and Simulation for Geologic Storage Projects, 2017, DOE, NETL

- Options for Risk Assessment tools for CCS projects are summarized in the table
- Risk assessors model the CCS system using one of these tools to predict risk (quantitatively or qualitatively)

Table 2-2: A Summary of Geologic Carbon Storage Risk Assessment Tools

Tool	Methodology Family
Carbon Storage Scenario Identification Framework (CASSIF), TNO	Qualitative, scenario-based
Vulnerability Evaluation Framework (VEF), U.S. EPA	Qualitative
Screening and Ranking Framework (SRF), LBNL	Qualitative, expert-elicited probabilities
CO2QUALSTORE guideline, DNV	Qualitative/Semi-quantitative, with "panel" inputs
Quintessa FEP database	Semi-Quantitative, FEPs screened by experts
TNO Risk Assessment Methodology	Semi-Quantitative, expert-elicited probability and consequence matrices
Risk Identification and Strategy using Quantitative Evaluation (RISQUE), URS	Semi-quantitative, expert-elicited probability and consequence matrices
CarbonWorkFlow Process for Long-term CO_2 Storage	Semi-quantitative, FEPs ranked through expert elicitation using a risk matrix approach
Performance Assessment (PA), Quintessa	Quantitative, evidence-support (three-valued) logic (ESL) Distinguishes cases of poor-quality data from uncertain data
CarbonSCORE software to pre-assess potential CO_2 storage sites	Quantitative, all evaluated criteria are weighted, jointly evaluated, and summarized
Oxand Performance & Risk (P&R™) Methodology	Quantitative, risk matrix evaluation
CO_2-PENS, LANL	Quantitative, hybrid system-process model
NRAP-IAM-CS	Quantitative, hybrid system-process model evolved from CO_2-PENS
Certification Framework (CF), LBNL	Quantitative, system-level model, probabilities partly calculated using fuzzy logic

BEST PRACTICES: Risk Management and Simulation for Geologic Storage Projects, 2017, DOE, NETL

- CO_2-PENS for example:
  - Risk assessment model that uses GoldWim (commercially available programming software)
  - CO2-PENS can be integrated with codes developed by other entities
  - Feed the model with inputs (e.g., storage reservoir characteristics, potential release mechanisms, flow transport model in porous media, potential receptors, etc.) → Output results are the Risk Levels

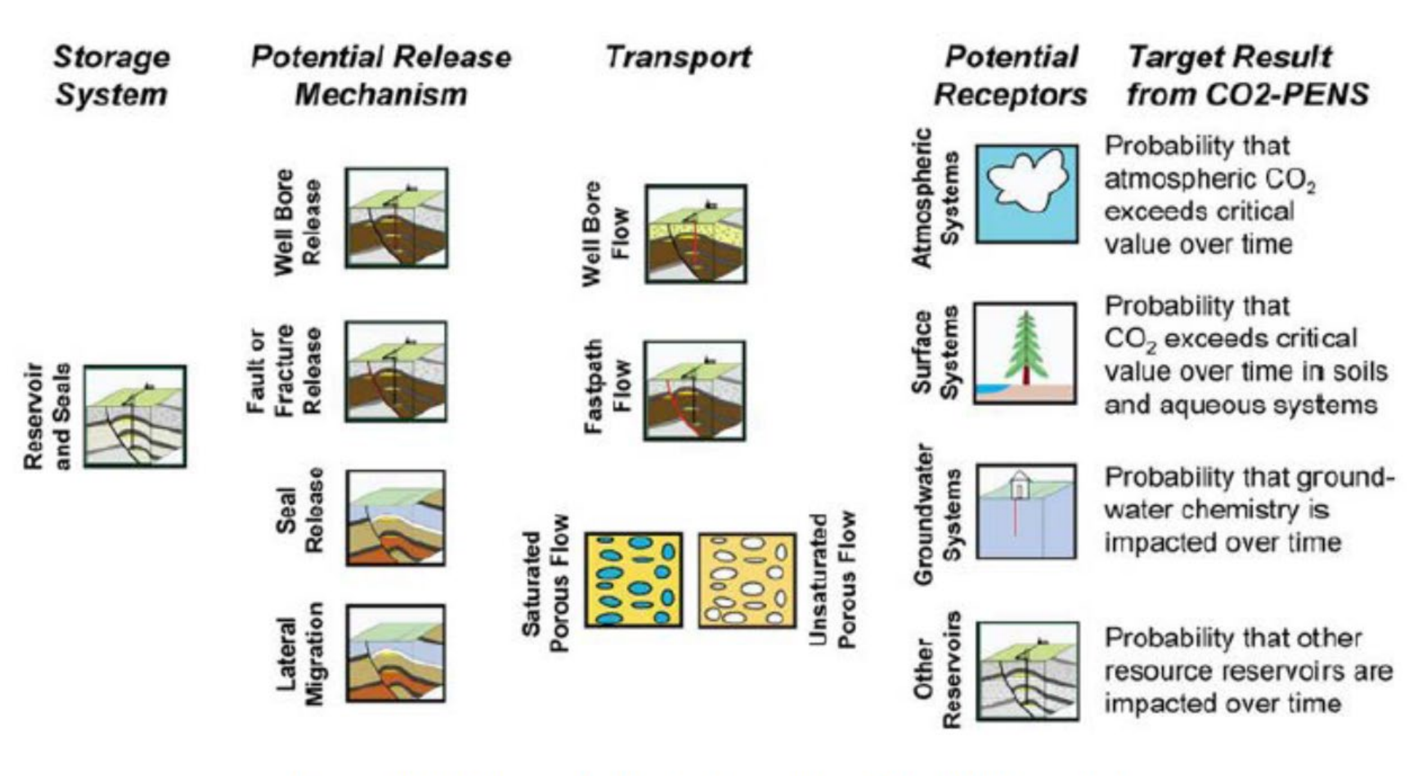


Figure 2-2: Schematic illustration of the CO_2-PENS model.

BEST PRACTICES: Risk Management and Simulation for Geologic Storage Projects, 2017, DOE, NETL

Ok, we conducted Risk Assessment and found some high potential risks of certain activities

- That does not mean to cancel the project
- It means to put in place risk mitigation strategies. Like what?

Table 5.7. Remediation options for geological CO_2 storage projects (after Benson and Hepple, 2005).

Scenario	Remediation options
Leakage up faults, fractures and spill points	• Lower injection pressure by injecting at a lower rate or through more wells (Buschbach and Bond, 1974); • Lower reservoir pressure by removing water or other fluids from the storage structure; • Intersect the leakage with extraction wells in the vicinity of the leak; • Create a hydraulic barrier by increasing the reservoir pressure upstream of the leak; • Lower the reservoir pressure by creating a pathway to access new compartments in the storage reservoir; • Stop injection to stabilize the project; • Stop injection, produce the CO_2 from the storage reservoir and reinject it back into a more suitable storage structure.

IPCC Special Report on Carbon Capture and Storage, 2005

Leakage through active or abandoned wells	• Repair leaking injection wells with standard well recompletion techniques such as replacing the injection tubing and packers; • Repair leaking injection wells by squeezing cement behind the well casing to plug leaks behind the casing; • Plug and abandon injection wells that cannot be repaired by the methods listed above; • Stop blow-outs from injection or abandoned wells with standard techniques to 'kill' a well such as injecting a heavy mud into the well casing. After control of the well is re-established, the recompletion or abandonment practices described above can be used. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and 'kill' the well by pumping mud down the interception well (DOGGR, 1974).

IPCC Special Report on Carbon Capture and Storage, 2005

Accumulation of CO_2 in the vadose zone and soil gas	• Accumulations of gaseous CO_2 in groundwater can be removed or at least made immobile, by drilling wells that intersect the accumulations and extracting the CO_2. The extracted CO_2 could be vented to the atmosphere or reinjected back into a suitable storage site; • Residual CO_2 that is trapped as an immobile gas phase can be removed by dissolving it in water and extracting it as a dissolved phase through groundwater extraction well; • CO_2 that has dissolved in the shallow groundwater could be removed, if needed, by pumping to the surface and aerating it to remove the CO_2. The groundwater could then either be used directly or reinjected back into the groundwate; • If metals or other trace contaminants have been mobilized by acidification of the groundwater, 'pump-and-treat' methods can be used to remove them. Alternatively, hydraulic barriers can be created to immobilize and contain the contaminants by appropriately placed injection and extraction wells. In addition to these active methods of remediation, passive methods that rely on natural biogeochemical processes may also be used.

IPCC Special Report on Carbon Capture and Storage, 2005

Large releases of CO_2 to the atmosphere	• For releases inside a building or confined space, large fans could be used to rapidly dilute CO_2 to safe levels; • For large releases spread out over a large area, dilution from natural atmospheric mixing (wind) will be the only practical method for diluting the CO_2; • For ongoing leakage in established areas, risks of exposure to high concentrations of CO_2 in confined spaces (e.g. cellar around a wellhead) or during periods of very low wind, fans could be used to keep the rate of air circulation high enough to ensure adequate dilution.

IPCC Special Report on Carbon Capture and Storage, 2005

Regulations and Permitting of CCS Projects

Permit needed?

- The main one is Class VI permit is needed to construct and operate CO_2 injection wells
- Other Environmental permits would also be required for CCS projects:
  - e.g., air quality permits, water quality permits, species and habitat and archeology related permits, and many more
  - How to determine the types of environmental permits needed?
    - The NEPA (National Environmental Policy Act) review process (if applicable) would generate and environmental assessment of the project and determines the types of environmental permits needed

So, here are the topics that we will discuss for this course module:

- At which stage of the project we need to seek Class VI permits?
- Class VI permit application (what information that goes into the application)
- Examples of other environmental permits that might apply to CCS projects
- The NEPA review process
  - Note: the NEPA review is conducted even before the permit applications

Let us get started…..

- At which stage of the project we need to seek class VI permits?
- Class VI permit application (what information that goes into the application)
- Examples of other environmental permits that might apply to CCS projects
- Discuss the NEPA review process

CCS Project Phases

	Regional Evaluation for a Specific Site	Site Selection & Characterization	Permitting	Operations	Post-Injection Monitoring	Long-Term Stewardship
Geologic Storage (GS) Class VI	Negative Cash Flow			Positive Cash Flow Injection Fee	Negative Cash Flow	Trust Fund Covers Costs
	• Volume of emissions to store and pore space needed. • Geologic, geophysical, engineering, financial, and social. • Identify several prospective sites. • Begin assembly of acreage block	• Assemble/acquire new data. • Drill new well(s) & acquire seismic. • Get necessary permits. • Finish assembling acreage block. • Prepare required plans for Class VI permit. • Front-end engineering design for site. • Establish financial responsibility.	• Submit all plans and financial responsibility for permit application. • Approval to drill injection wells; State approves site permit. • Drill injection wells, incorporate new data in plans (e.g., AoR) and present to Director of EPA. • Injection operations approved. • Have 180 days to submit monitoring, reporting and verification (MRV) plan per Subpart RR regulations.	• Finish construction of surface facilities and MVA grid. • Begin injection of captured CO_2. • Follow plans, AoR every 5 years, annual reporting. • Annual mechanical integrity testing. • Drill new monitoring wells/perform corrective action as plume expands. • Plug and abandon (P&A) injection wells per plan. • Some financial responsibility instruments released.	• Update & present post-injection site care & site closure plan to Director. • Apply for reduced time period. • Follow Post-Injection Site Care (PISC) & site closure plan. • Plugged and abandoned all wells, restore sites. • Release of financial responsibility instruments.	• Another entity accepts long-term stewardship, oversees trust fund, pays site costs, settles all claims.
	0.5 to 1 year	3+ years	2+ years	30 to 50 years	10 to 50+ years	Post Closure

Carbon Storage Atlas 5th Edition, DOE’s NETL, https://www.netl.doe.gov/sites/default/files/2018-10/ATLAS-V-2015.pdf

Next……

- At which stage of the project we need to seek Class VI permits?
- Class VI permit application (what information that goes into the application)
- Examples of other environmental permits that might apply to CCS projects
- Discuss the NEPA review process

- A LOT of information needs to be submitted → it is a comprehensive permit application

BEST PRACTICES: Operations for Geologic Storage Projects, 2017, DOE, NETL

What does a Class VI Permit application includes? →

- The application presents detailed evaluation of the:
  - Site geology and site characterization data (e.g., groundwater quality, well logs, core samples, site maps)
  - Well design, construction, operating conditions, monitoring plan, and closure and post-closure plans
  - AoR (the region where the USDW is endangered") and computational modeling results to predict CO_2 plume transport within the AoR
    - Note: the AoR is re-evaluated periodically (every 5 years by default and prior to site closure). The initial AoR serves as a benchmark and the purpose of the periodic re-evaluation is to ensure CO_2 plume is behaving as predicted.
  - Corrective action plans
  - Emergency and remedial response plans
  - Financial responsibility: For what?
    - To finance corrective action, well plugging and site closure, emergency and remedial responses. This ensures that taxpayers will not have to pay for these expenses if the applicant becomes financially insolvent

BEST PRACTICES: Operations for Geologic Storage Projects, 2017, DOE, NETL

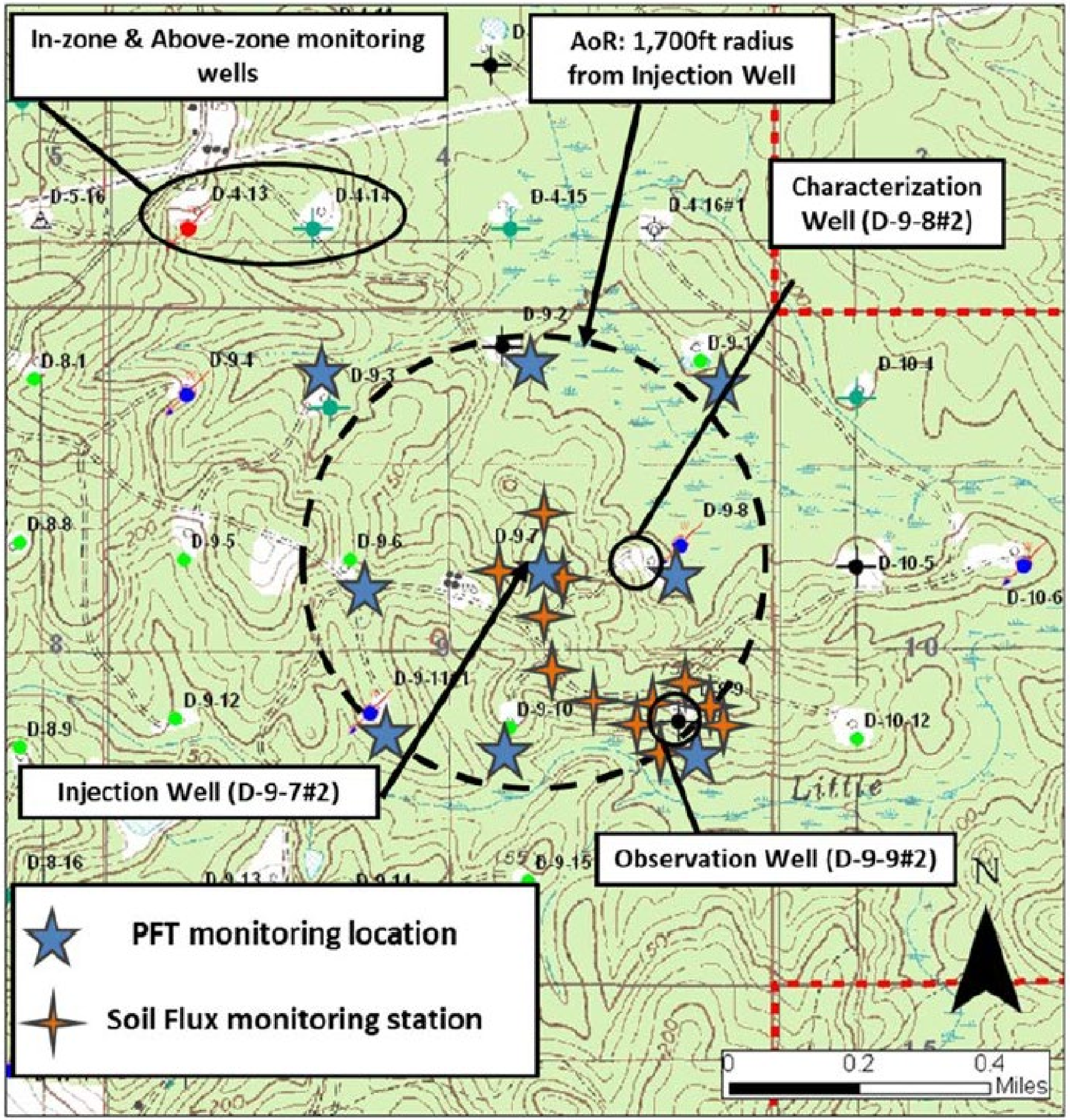


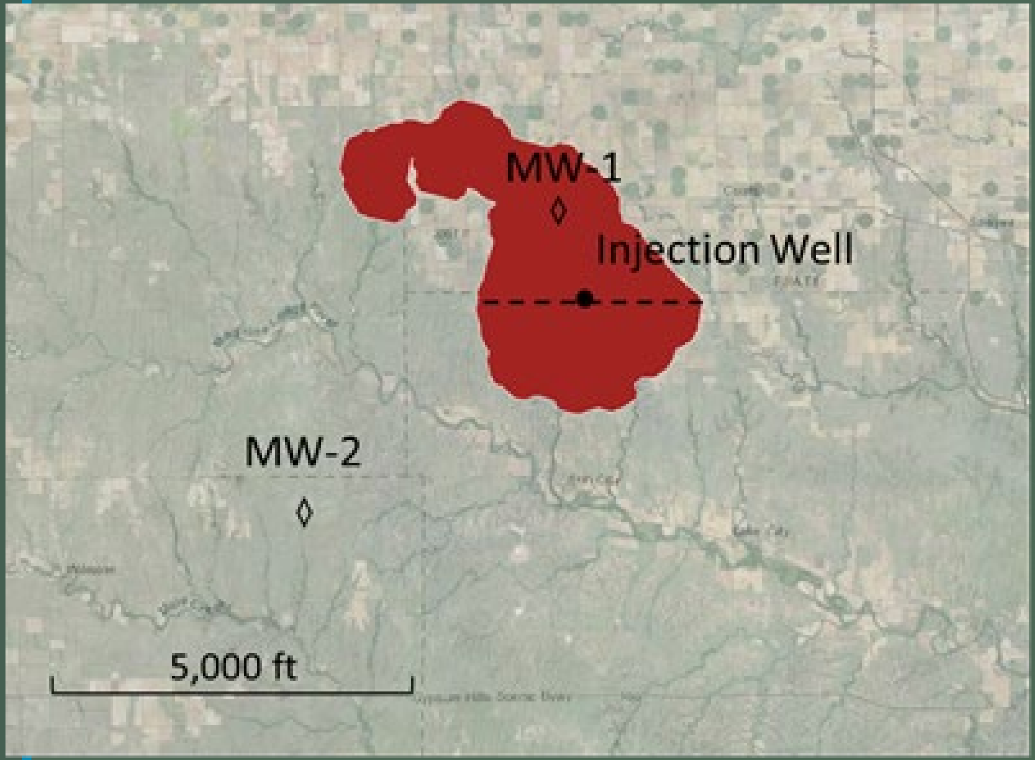
Figure 3-1: Area of Review for the SECARB Citronelle Project Site. Figure shows the location of the injection well, observation wells, and all monitoring locations.

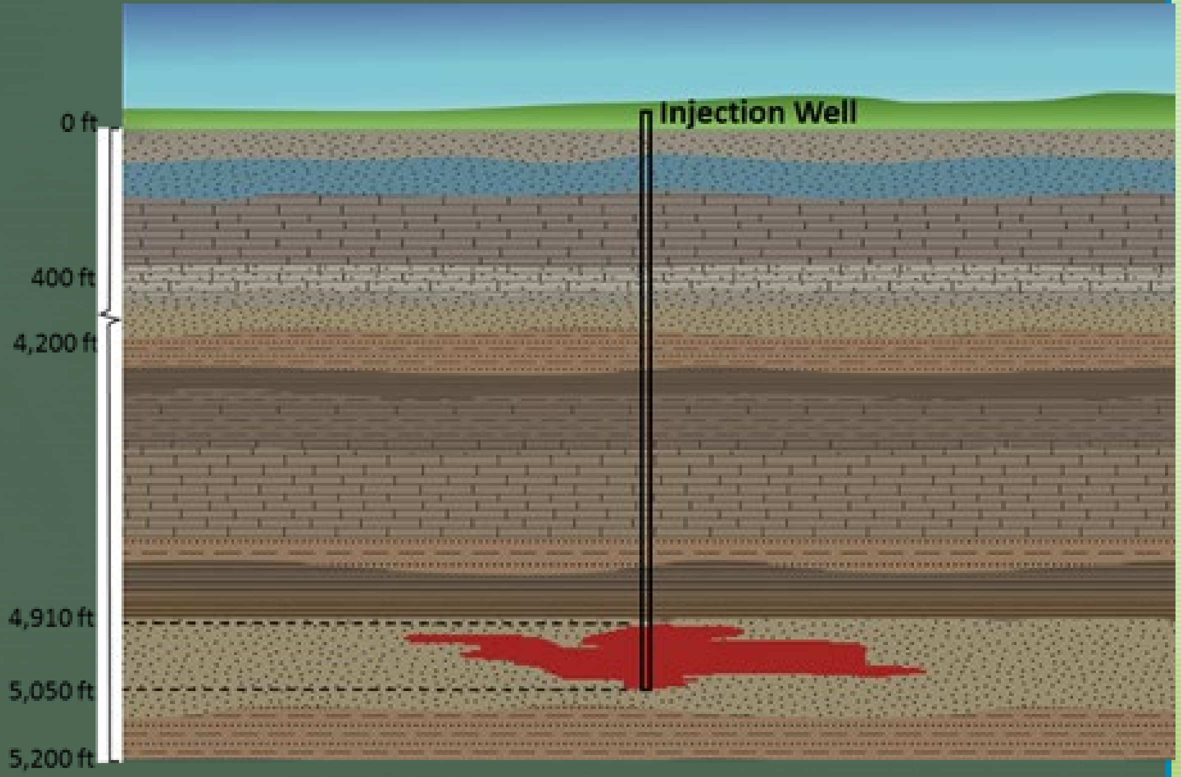
Table 3-1: Typical Injection Permit Information Provided by RCSPs

Information Typically Provided by RCSPs*
Geologic Information
• Injection Depth and Formation • Lithological Description • Lower-Most USDW • Testing of Multiple Sources of Groundwater • Model of Potential Plume Development
Well Design and Construction
• AoR Detailed Schematic and Proposal • Legal Description of Land Ownership • Proof of Notification of Injection Intent to Affected Parties in the Region • Third Party Certifications for Injection and Construction • Construction details on all wells within the AoR and remediation action taken to improve these wells, if necessary
Description of Surface Equipment
• Proposed Equipment to be Installed • Equipment Sizing and Location Calculations • Proposed Average and Maximum Daily Rate of Fluids to be Injected • Proposed Average and Maximum Surface Injection Pressure • Potential Fracture Pressure Determination
Monitoring Systems
• Continuous Sampling of Multiple Neighboring Drinking Water Wells • Proposed Injection Monitoring Plan Equipment • Post-Injection Long-Term Monitoring Plan and Equipment
Logging and Testing Results
• Geophysical Data Supporting Location of Injection Zone and Caprocks and Absence of Resolvable Faults • Modeling of AoR Throughout Pre-Injection, Injection, and Long-Term Post-Injection

Geologic Storage Projects, 2017, DOE, NETL

- Example modeling results to show the extent of CO_2 plume (plan and cross section)





https://cadmusgroup.com/articles/permitting-framework-for-geologic-sequestration-wells/

Next…...

- At which stage of the project we need to seek Class VI permits?
- Class VI permit application (what information that goes into the application)
- Examples of other environmental permits that might apply to CCS projects
- Discuss the NEPA review process

Table 1. Overview of types of permits and permissions needed for CCUS projects

Portion of the CCUS effort *	Authorization	Authorities that may require permits/permissions	Type of Agency**
	Land use	Local government, Federal Government (public lands)	City Council, Federal Land Manager (USFS, BLM, etc.)
	Discharges to surface water	State and/or Federal Government	State Department of Environmental Quality, U.S. Environmental Protection Agency
	Discharge of dredge or fill materials to waters of the U.S.	State and/or Federal Government	U.S. Army Corps of Engineers and or relevant State office (Florida, Michigan and New Jersey)
	Endangered species	State and/or Federal Government	State Environmental or Natural Resources Department, U.S. Fish and Wildlife Service, NOAA Fisheries
	Greenhouse gas reporting	State and/or Federal Government	State Environmental Department, U.S. Environmental Protection Agency
	Air permits	State and/or Federal Government	State Environmental Department, U.S. Environmental Protection Agency
	CO_2 pipeline safety	State and/or Federal Government	State and Federal Departments of Transportation
	Siting CO_2 pipelines	Local, State, and Federal Government	State Transportation Department or Utility Commission; Federal land management agencies
	Pore space ownership and mineral rights	Local, State, and Federal Government (if Federal lands)	Determined by State-specific law, Federal agency managing Federal Lands to be used
	CO_2 injection (and sequestration) permitting	State and/or Federal Government (some states have primacy for Class VI permitting)	State Environmental Department, U.S. Environmental Protection Agency

denotes utilization, denotes capture, denotes transportation, and denotes geologic sequestration

**Federal responsibility is listed together with exemplary state and local governments (which vary depending on local context). For Tribal lands/sovereign nations, the Tribal government will have oversight.

- This table covers all CCS project components (capture, pipelines, utilization and sequestration)

Air quality regulators would be involved mainly with:

- Air permits for the capture and utilization portion of the CCS project
- Greenhouse Gas Reporting for all four aspects of the project (capture, utilization, storage and transport

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

Air Quality Permits Relevant to CCS Projects

- The CO_2 capture and utilization components of the CCUS projects may require Title V permits and New Source Review

Federal Permit or Review	Agency	Agency Point of Interaction	Type of Project*	Summary of Permitting/Review and Responsibility	Authority
Clean Air Act Title V Operating Permit	Environmental Protection Agency for states, territories, or tribes that do not have EPA-approved programs or delegated authority	EPA Regional Office for states, territories, or tribes that do not have EPA-approved programs or delegated authority		A Title V Operating Permit is required for any "major source" and certain other sources. A major source has actual or potential emissions at or above the major source threshold for certain air pollutants. In air quality attainment areas, the major source threshold is 100 tons/year, while lower thresholds may apply in non-attainment areas (for the pollutant that is in non-attainment). Major source thresholds for hazardous air pollutants (HAP) are 10 tons/year for a single HAP or 25 tons/year for any combination of HAP. Also, sources with a Major Source permit under the New Source Review (NSR) permitting program are required to obtain a Title V permit. The Title V operating permit generally does not add new requirements for the facility; rather, it contains emission limitations and other conditions as necessary to assure compliance with all air quality control requirements or "applicable requirements" required under the Clean Air Act (e.g., New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), State Implementation Plans (SIP), and NSR), and it requires that certain procedural requirements be followed.	42 U.S.C. § 7661 et seq; 40 CFR Parts 70, 71
Prevention of Significant Deterioration (PSD) / New Source Review (NSR)	Environmental Protection Agency for states, territories, or tribes that do not have EPA-approved programs or delegated authority	EPA Regional Office for states, territories, or tribes that do not have EPA-approved programs or delegated authority		Prevention of Significant Deterioration (PSD) permits are required for new major stationary sources or major modifications for pollutants where the area the source is located is in attainment or unclassifiable with the National Ambient Air Quality Standards (NAAQS). Nonattainment NSR (NNSR) permits are required for new major stationary sources or major modifications in areas that do not meet one or more of the NAAQS. A minor NSR permit is required for any new or modified source of air pollutant that emits lower than the major NSR emission thresholds and, thus, is not subject to PSD or NNSR permitting.	42 U.S.C. §§ 7470-7479, 42 U.S.C. §§ 7501-7503; 40 CFR parts 49, 51, and 52

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

Compressors also need permits – Here is and example from Pennsylvania

Table 1. Compressor station regulation. The following matrix is provided as a basic overview of compressor station parameters that are regulated and the agencies involved.

	Gathering System Compressors (PA)		Interstate System Compressors (Federal)	
	Agency	Regulation	Agency	Regulation
Air Emissions	PA DEP	Revised GP-5 permit	EPA and PA DEP	Clean Air Act
Noise Emissions	None*	*Municipalities may have local noise ordinances that would apply to compressor stations within the municipality		Noise must not exceed a day-night average level of 55 decibels at any preexisting noise-sensitive area (NSA) such as schools, hospitals, or residences
Erosion and Sedimentation	PA DEP	Chapter 102: erosion and sediment pollution control regulations	FERC	FERC works in cooperation with county Conservation Districts to implement these regulations
Siting	PA DEP (limited)	Chapter 105: waterways and wetlands permitting	FERC	FERC scoping, environmental review, and public input
Vibration	None		FERC	Companies are required to comply with FERC's rule at 18CFR 380.12(k)(4)(v)(B) to ensure there is no increase in perceptible vibration from the operation
Operation, Maintenance and Safety	PA PUC	Material and design specifications, on-site inspections, review of maintenance and safety	US DOT PHMSA	Material and design specifications, on-site inspections, review of maintenance and safety

https://extension.psu.edu/understanding-natural-gas-compressor-stations

The Greenhouse Gas Reporting Program (GHGRP)

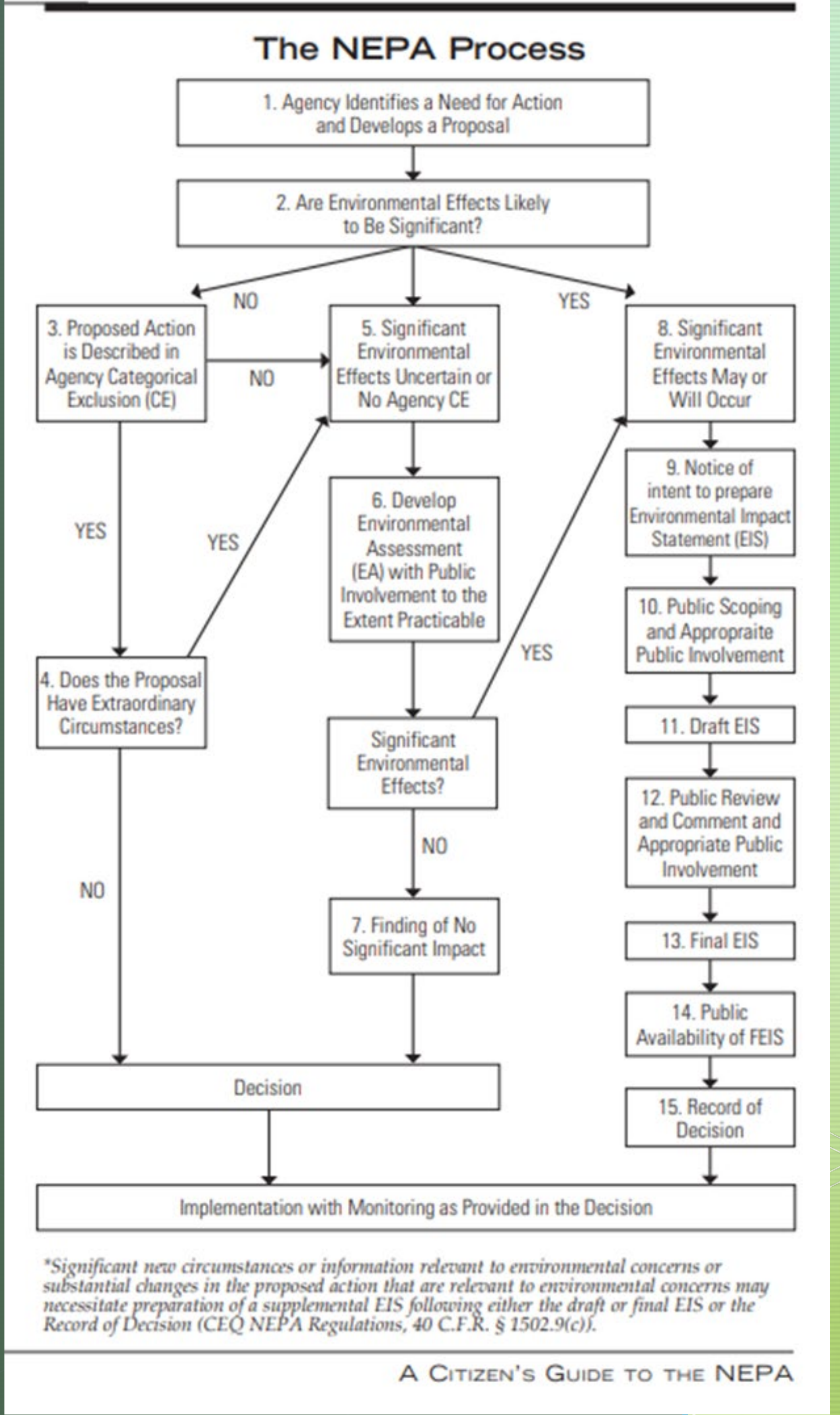
- GHG emissions from large emission sources, fuel and gas supplies, and CO_2 injection sites must be reported under the US EPA's GHGRP.
- The GHGRP has different subparts that apply to different components of the CCS project.
    - Subpart RR: applies to geologic sequestration (not EOR) – the facilities need to report *how much they sequester*
    - Subpart PP: applies to facilities that capture CO_2 from industrial sources
    - Subpart UU: applies to EOR facilities, acid-gas injection facilities, CO_2 storage RESEARCH and DEVELOPMENT (not commercial sequestration projects)
    - *So, in general under this program, facilities report info. on CO_2 received for injection, the amount of CO_2 sequestered, and annual monitoring activities*
- The GHGRP data is public data (~8000 facilities in the US have to report GHG data every year).

Last……

- At which stage of the project we need to seek VI permits?
- Class VI permit application (what information that goes into the application)
- Examples of other environmental permits that might apply to CCS projects
- Discuss the NEPA review process

The NEPA Review

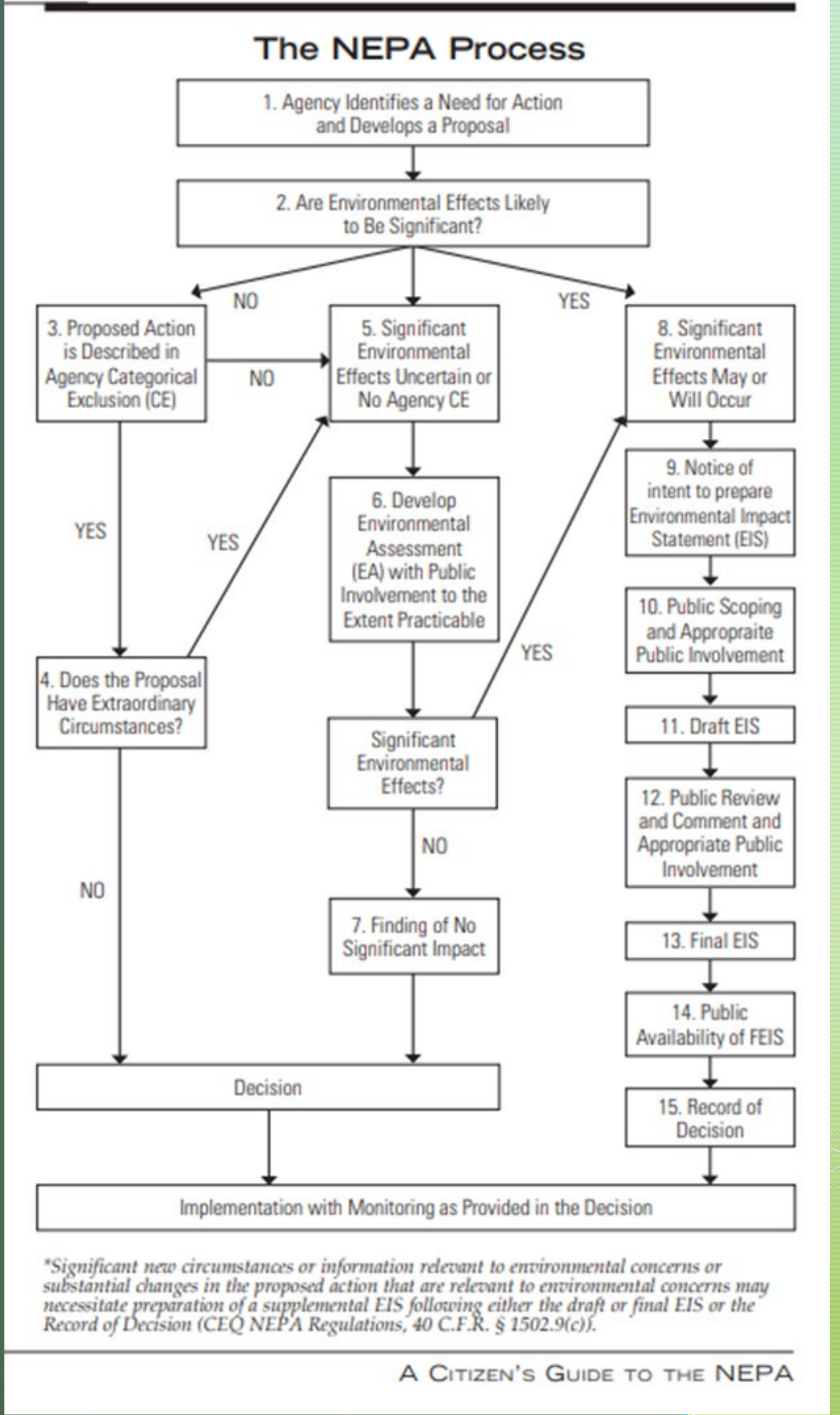
- The National Environmental Policy Act (NEPA) law was enacted in 1970
- NEPA requires environmental, economic, social, and cultural impact review of projects that involve major federal action (e.g. funding, or built on federal land)
- The Federal agency conducts an Environmental Assessment (EA) of the proposed CCS project.



The Department of Energy (DOE) takes the lead on NEPA review for CCS projects

Back to NEPA Review process

- The National Environmental Policy Act (NEPA) law was enacted in 1970
- NEPA requires environmental, economic, social, and cultural impact review of projects that involve major federal action (e.g. funding, or built on federal land)
- The Federal agency conducts an Environmental Assessment (EA) of the proposed CCS project.
- What does EA do?
  - Evaluates the need for the proposed project
  - Identifies and evaluates reasonable alternatives
  - Evaluate the environmental, social, economic, and cultural impacts of the proposed project



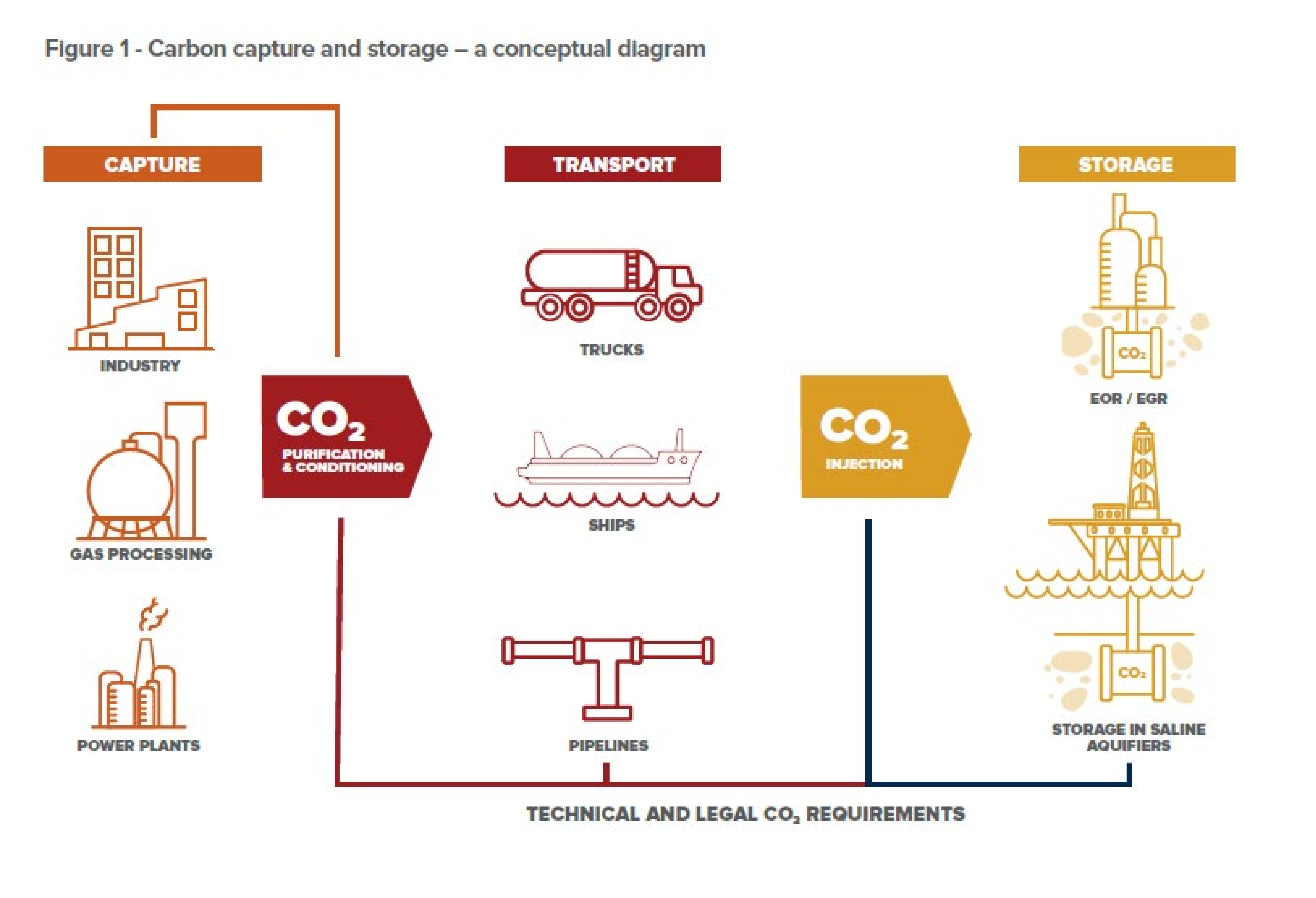
- If the EA concludes that the proposed project has potential "significant" impacts → then a more detailed assessment must be prepared called "Environmental Impact Statement (EIS) – this involves public review of the project

- How is "significant" impact is defined in NEPA? →

  - By considering context (i.e., the scope of the proposed action) and intensity (beneficial and adverse impact, effect on public health and safety, unique characteristics of the geographic area like proximity to cultural resources, parkland, or other critical issues, the degree to which the effects are likely to be controversial)

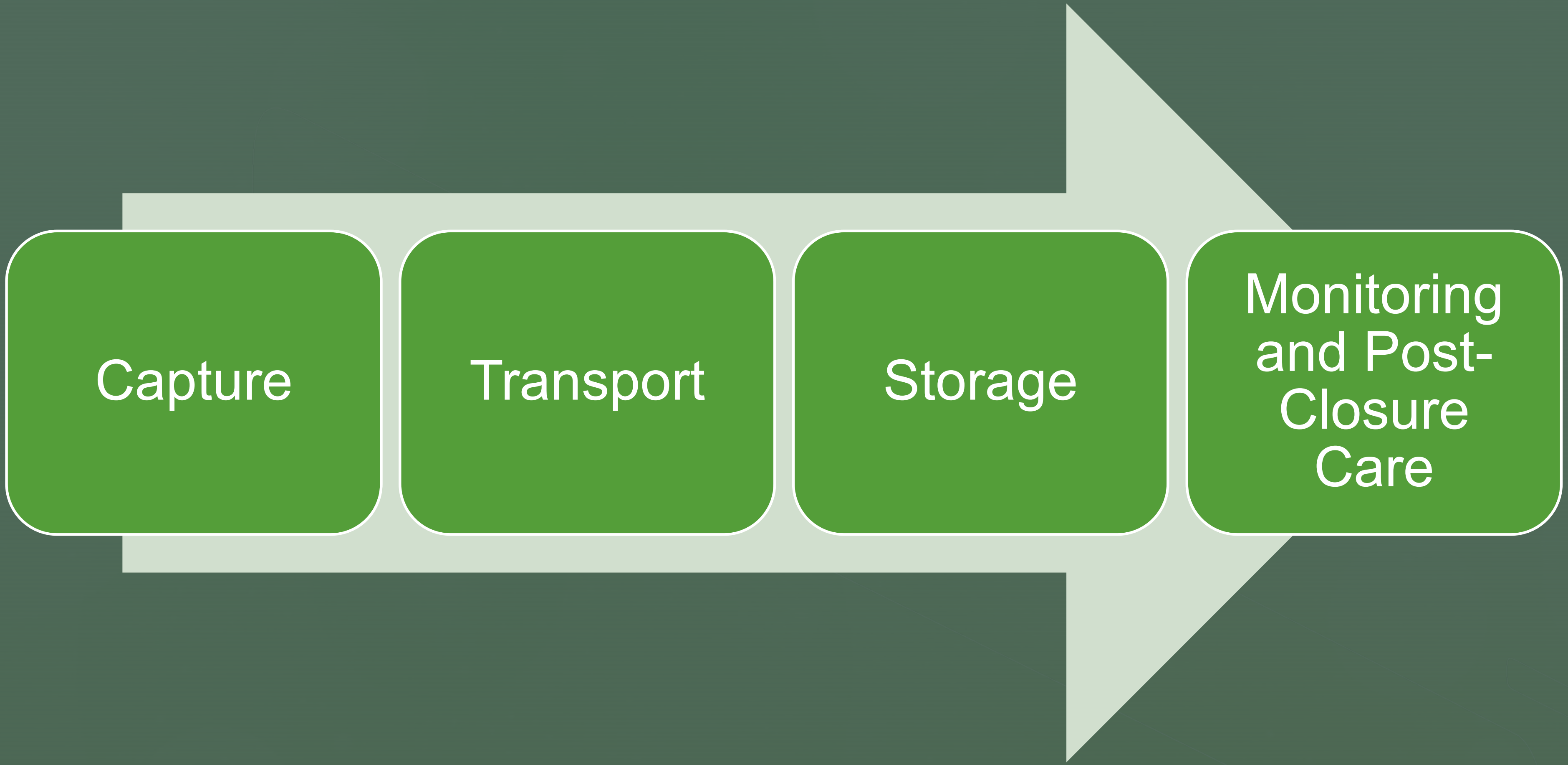
- The *Council on Environmental Quality (CEQ) oversees NEPA implementation*

Cost and Technology Readiness of CCUS



Technology Readiness and Costs of CCS, 2021, Global CCS Institute

Cost $??

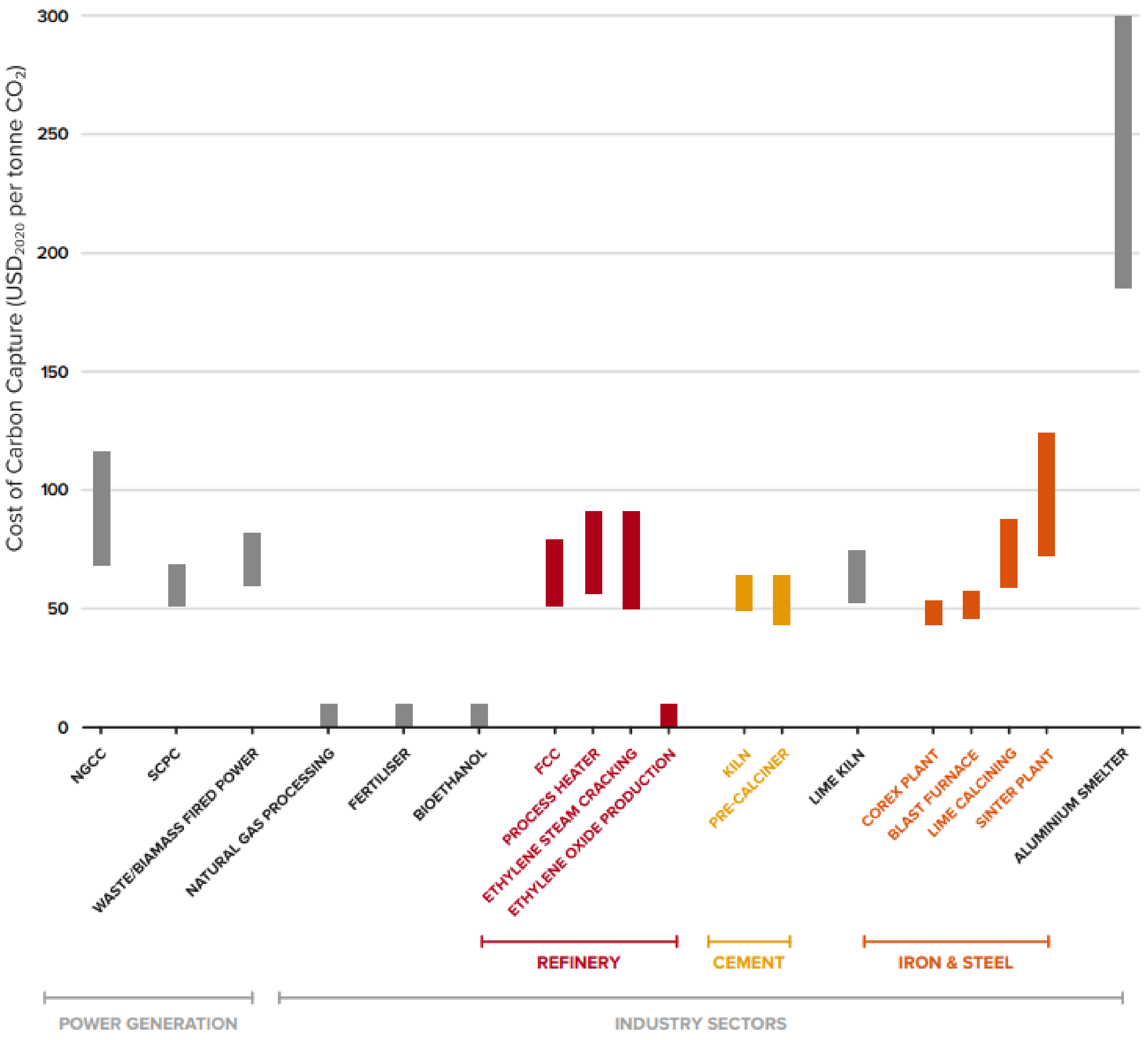

Capture
Transport
Storage
Monitoring and Post-Closure Care

- There are a lot of cost number out there.
- The cost data presented hereafter are obtained om this 2021 report.
- In any cost estimation study → there are a lot of assumptions made to get the costs and the cost is always a range (project-specific).

Capture Cost

- NGCC = Natural gas-fired combined-cycle plant
- Please see the graph and I would ask in the next slide that you share one observation you have on this graph

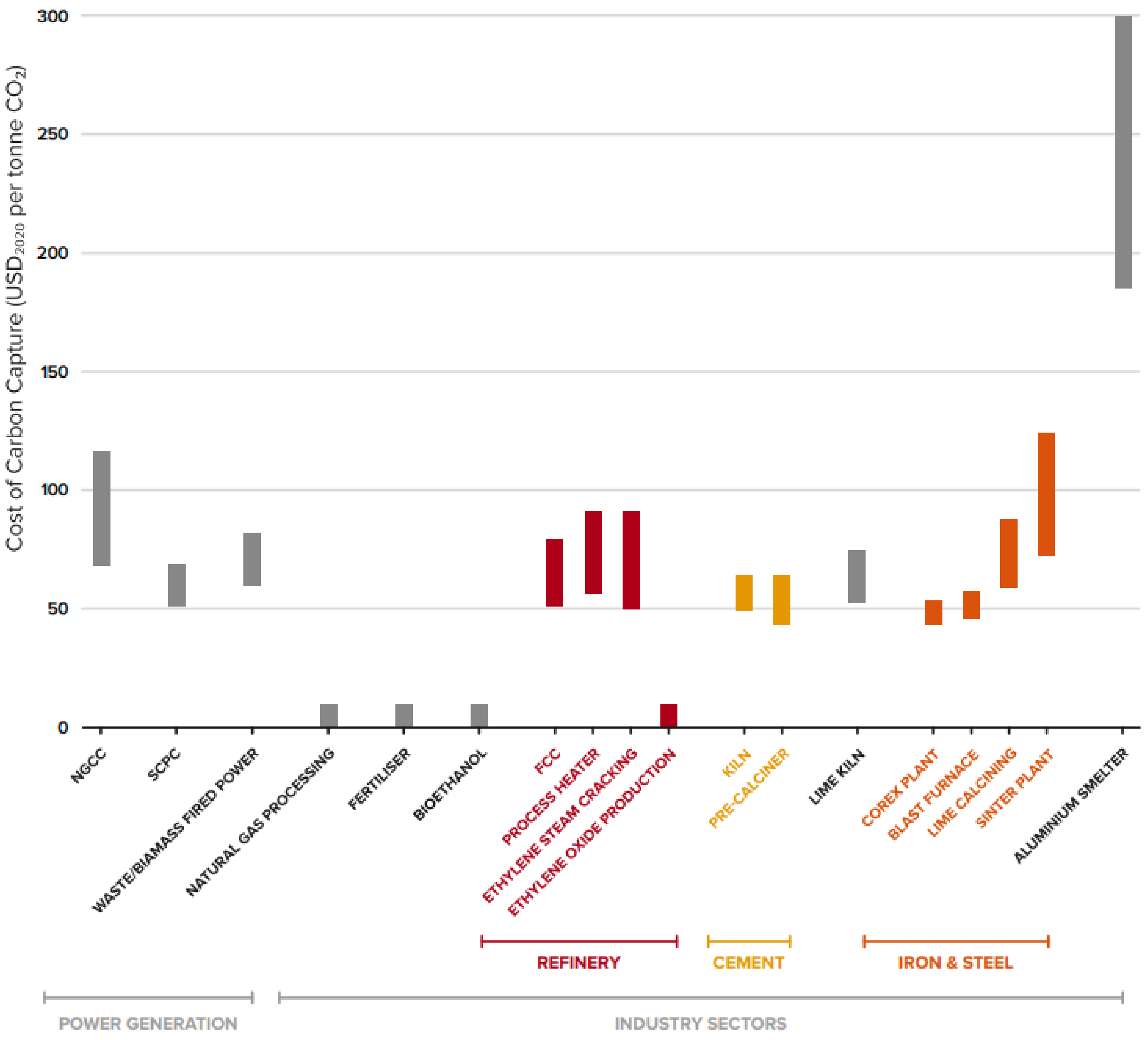
Figure 12 - Cost of carbon capture in various types of power and industrial processes, excluding downstream CO_2 compression.[4]



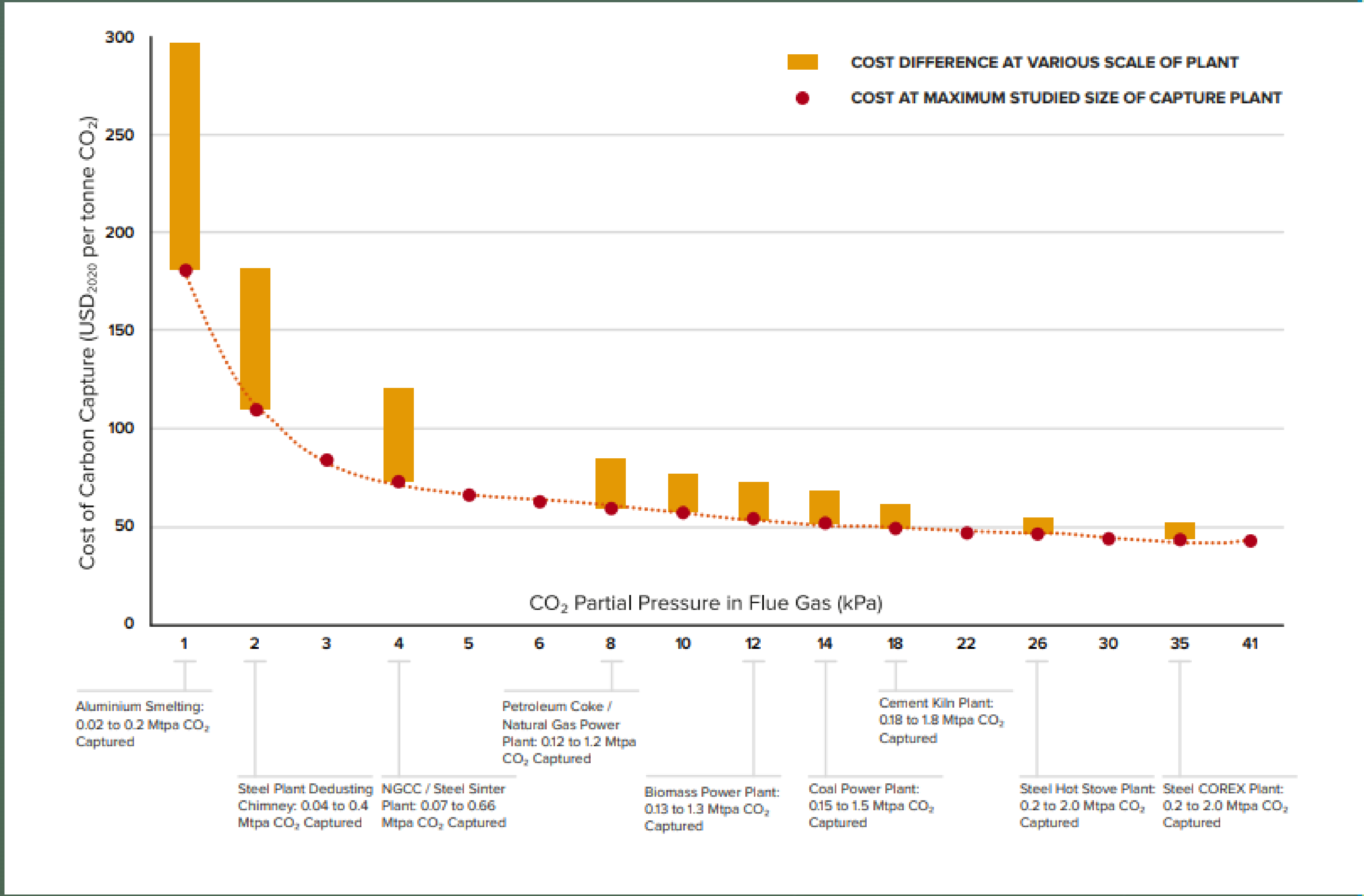
Capture Cost

- What stood out to me that aluminum smelter was on a different scale (much higher than others)

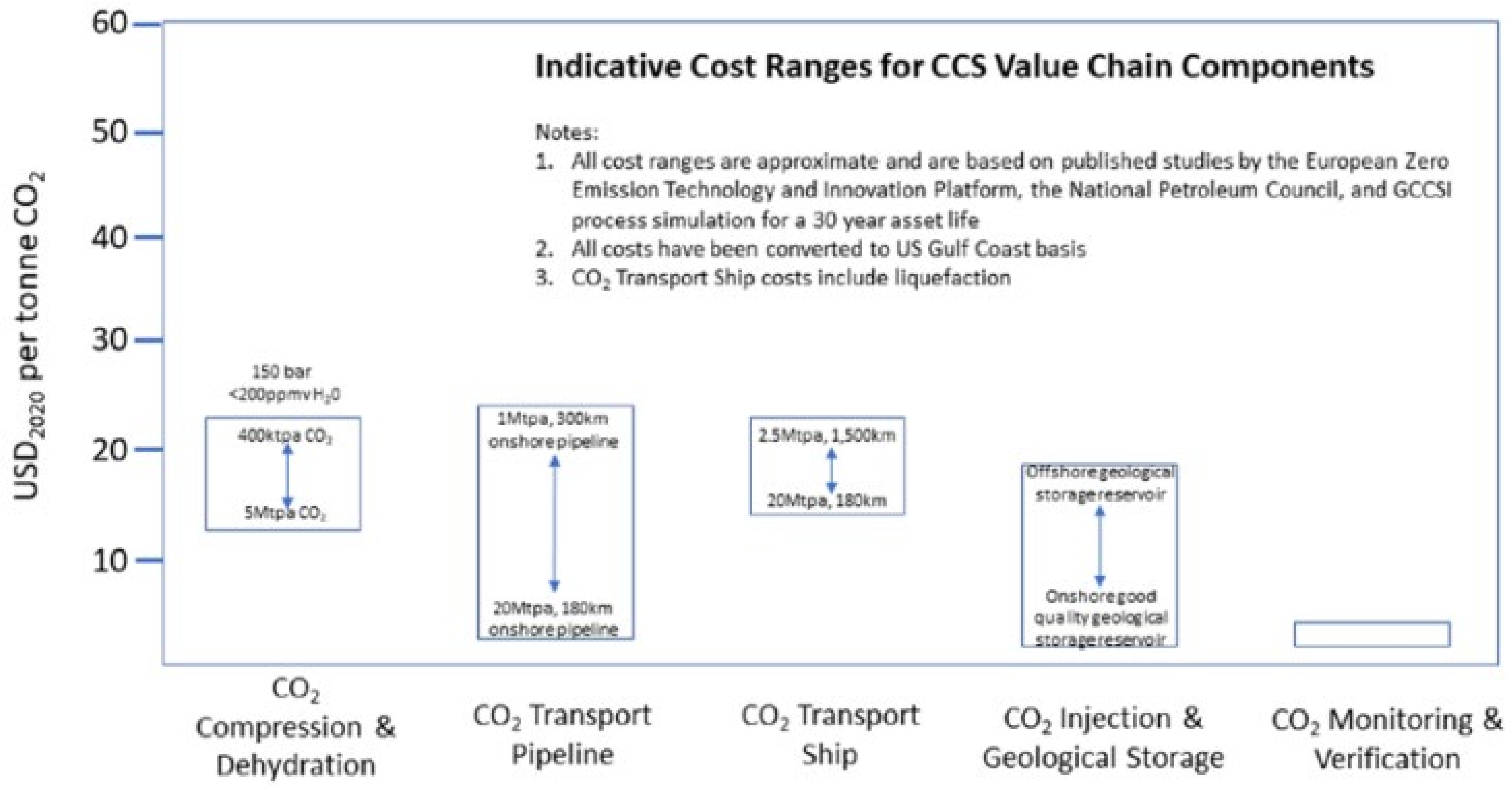
Figure 12 - Cost of carbon capture in various types of power and industrial processes, excluding downstream CO_2 compression.[4]



Translation ☺ → Always look for CO_2 partial pressure



Costs of the rest of the processes: Compression, dehydration, Transport, Storage and Monitoring



[7] Based on GCCSI process simulation and analysis of: ZEP 2019, The cost of subsurface storage of CO_2, ZEP Memorandum, December 2019. IEAGHG ZEP 2011, The Costs of CO_2 Storage, Post-demonstration CCS in the EU. National Petroleum Council 2019, Meeting the Dual Challenge, A Roadmap to at-scale deployment of carbon capture use and storage. National Petroleum Council 2019, Topic paper #1, Supply and Demand Analysis for Capture and Storage of Anthropogenic Carbon Dioxide in the Central US.

Let us add it all up - example scenario (I used the average values)

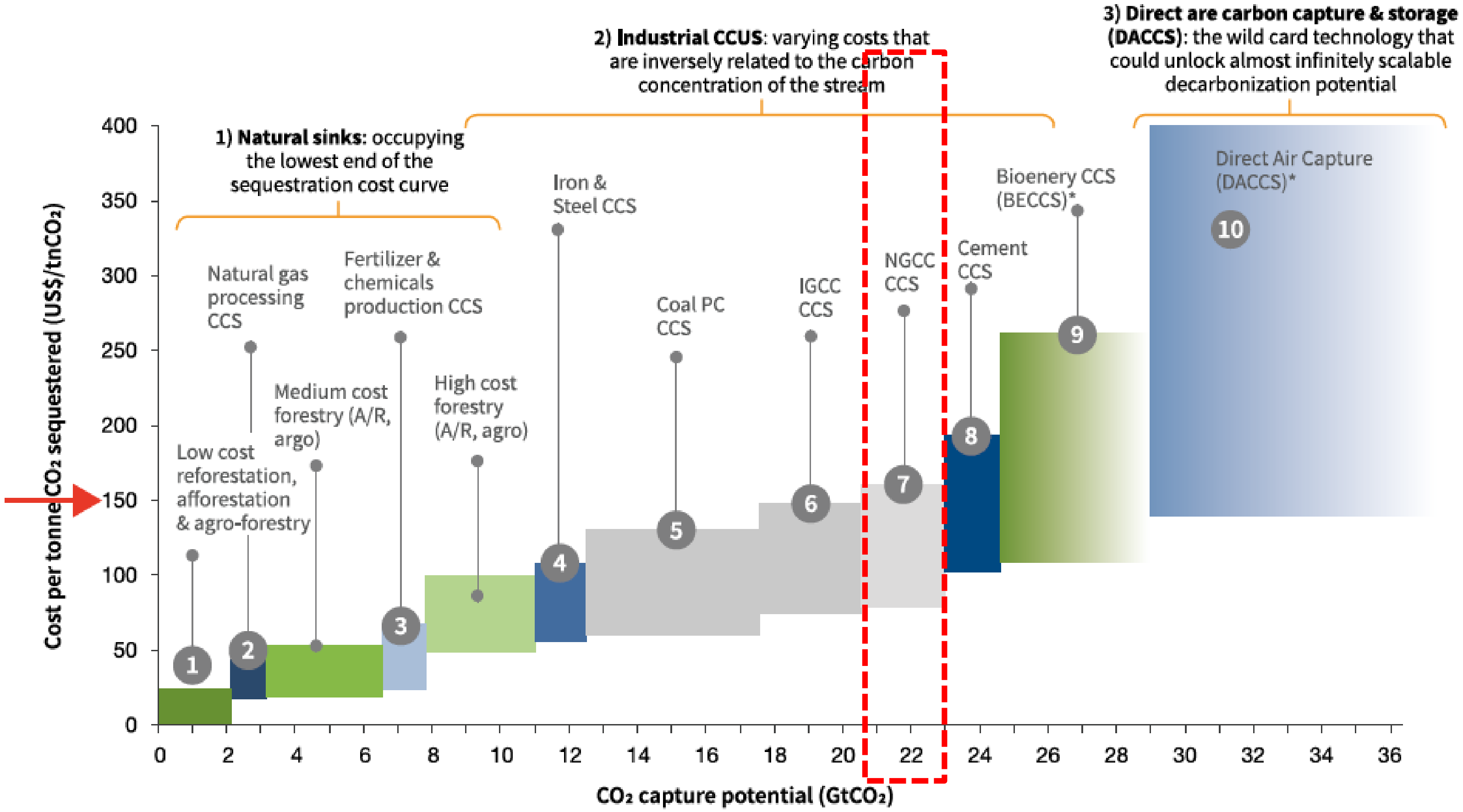
Item	$/ton CO_2 removed
Capture (NGCC power plant)	80
Compression and dehydration	15
Pipeline transport	15
Storage	10
Monitoring and verification	5
Total	$125/ton CO_2 removed

- Capturing is the most expensive part → will be much cheaper for industry like bioethanol
- These costs do not include the 45Q or LCFS credits

Here is another cost graph that agrees with the previous information (shows the total cost of CCS – not individual components)

- NGCC cost is in the range of what we calculated
- DA-CCS is the highest → It is all about the CO_2 partial pressure

Figure 6.1 Carbon sequestration cost curve (US$/tn CO_2 eq) and the GHG emissions abatement potential ($GtCO_2$ eq)

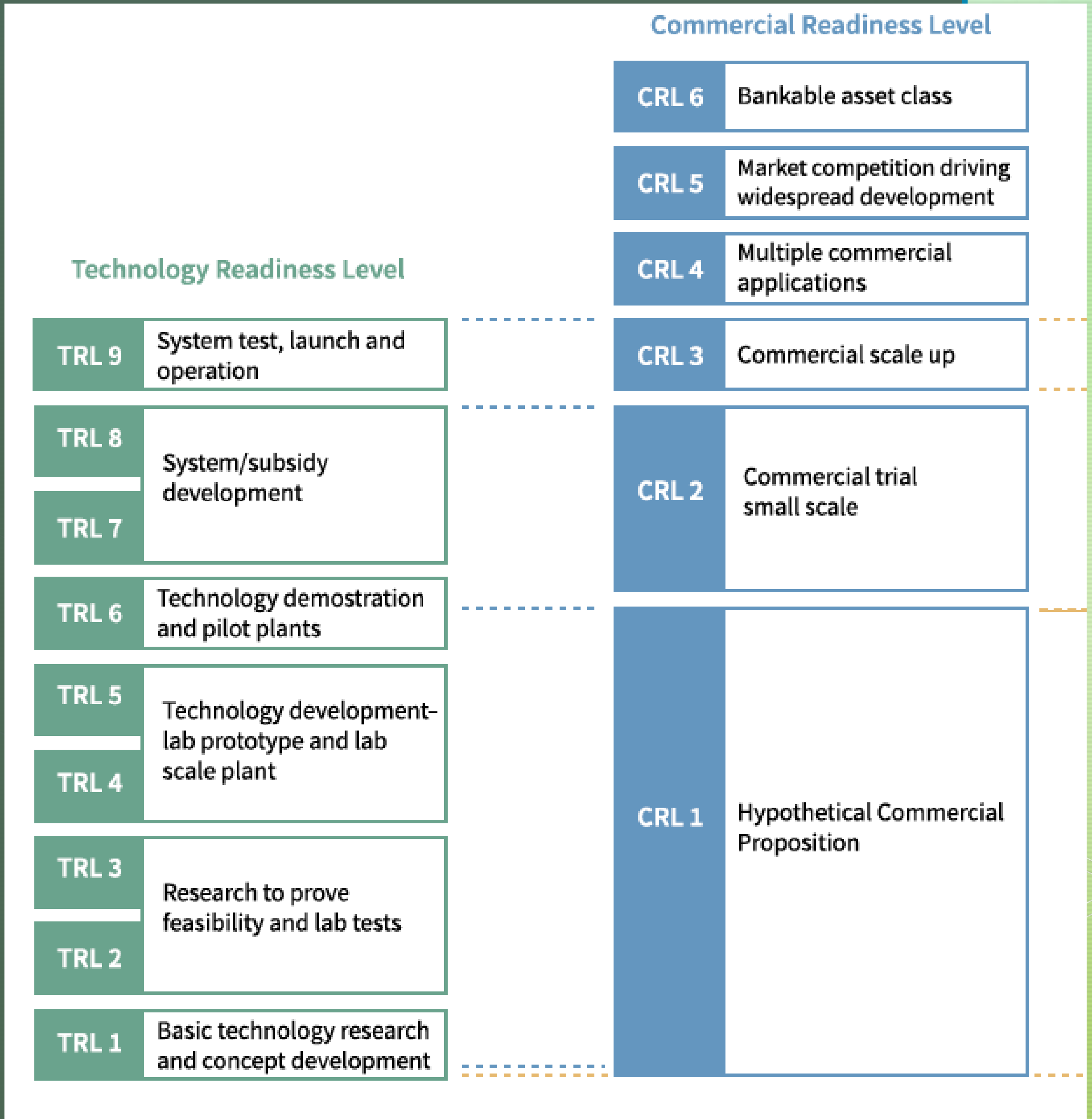


*Indicates technologies still in early (pilot) stage of development

Source: Goldman Sachs, Equity Research 2020

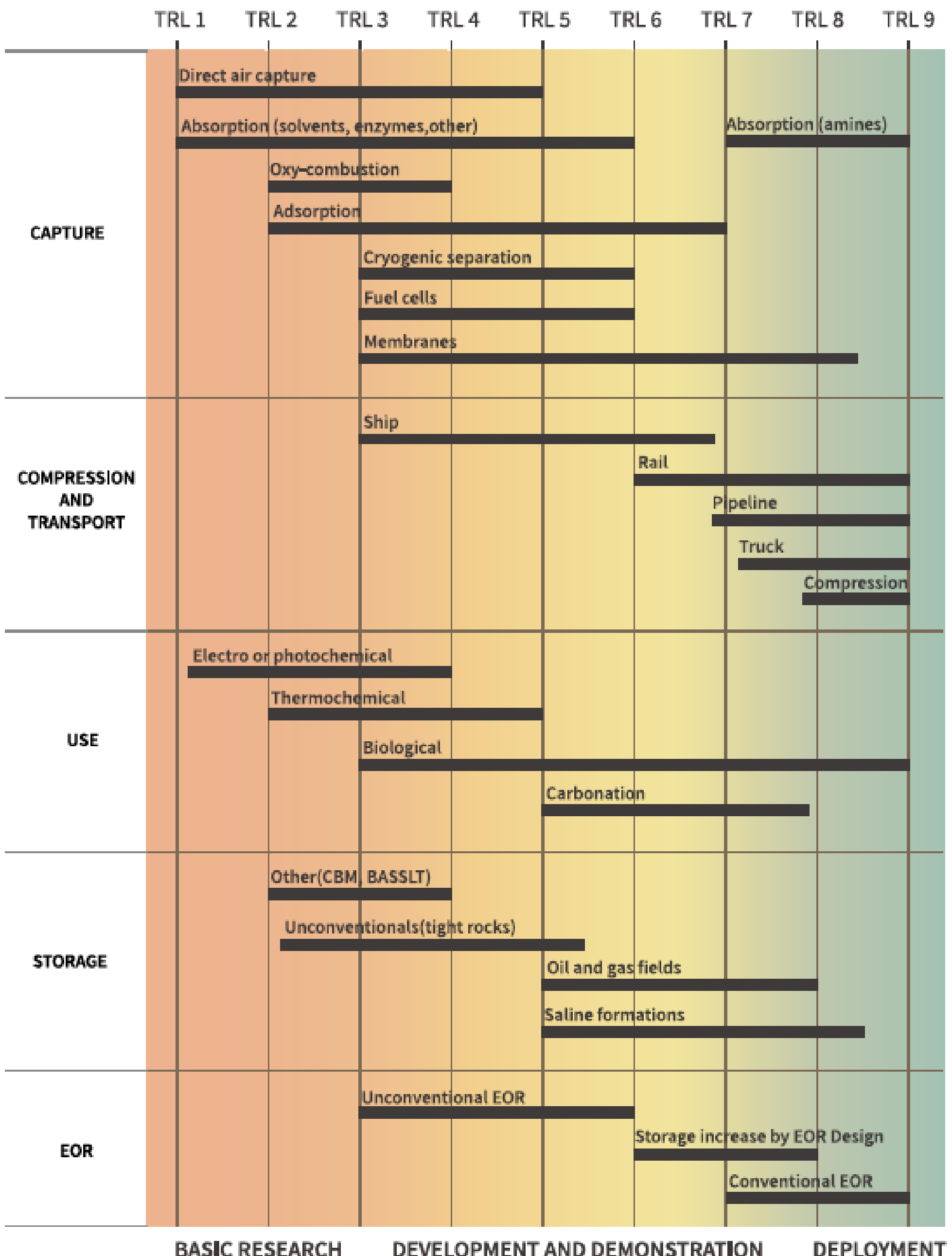
Technology Brief, CARBON CAPTURE, USE AND STORAGE (CCUS), UNECE

Technology Readiness Level

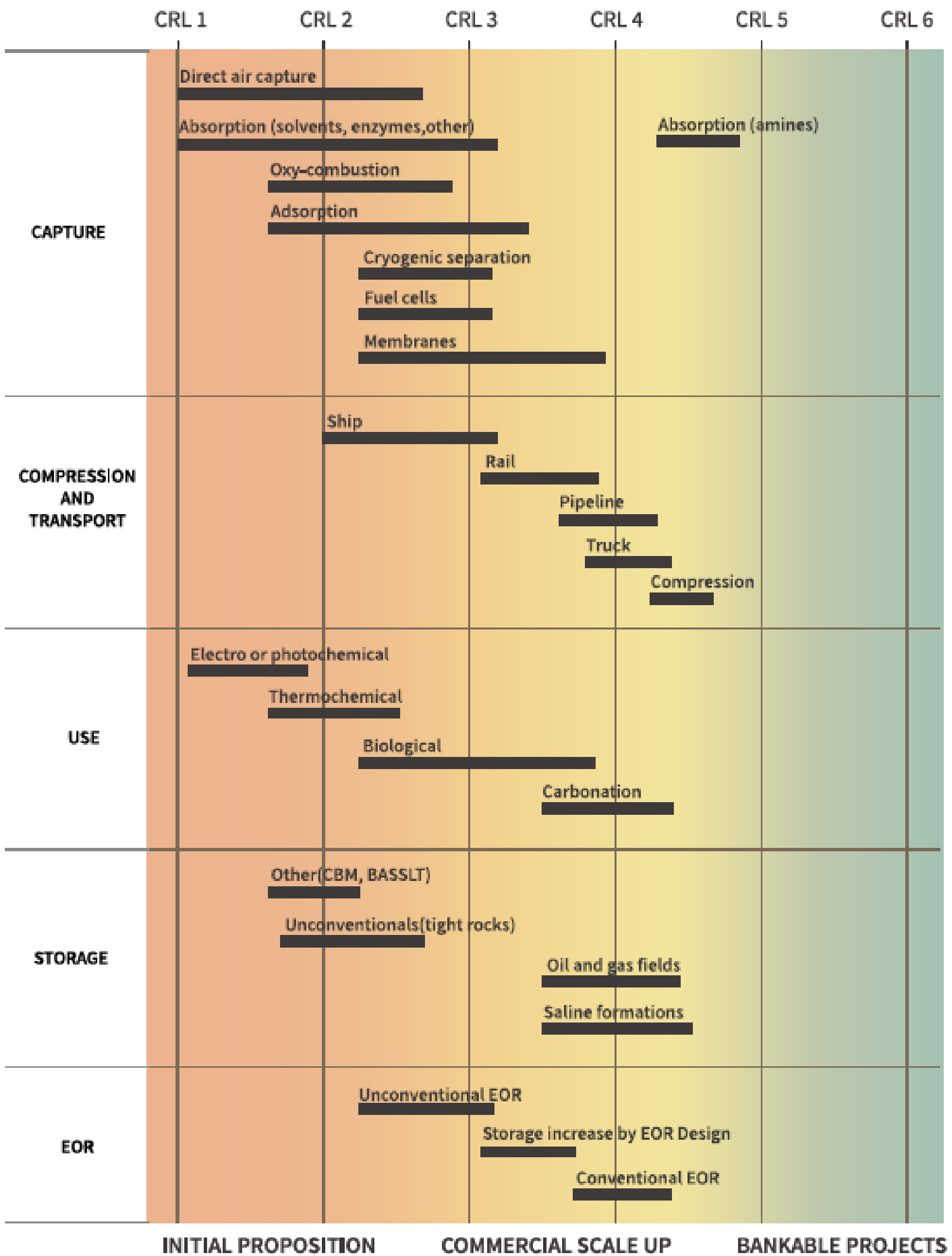


https://unece.org/sites/default/files/2021-03/CCUS%20brochure_EN_final.pdf https://unece.org/sites/default/files/2021-03/CCUS%20brochure_EN_final.pdf

Technology Readiness Level



Commercial Readiness Level

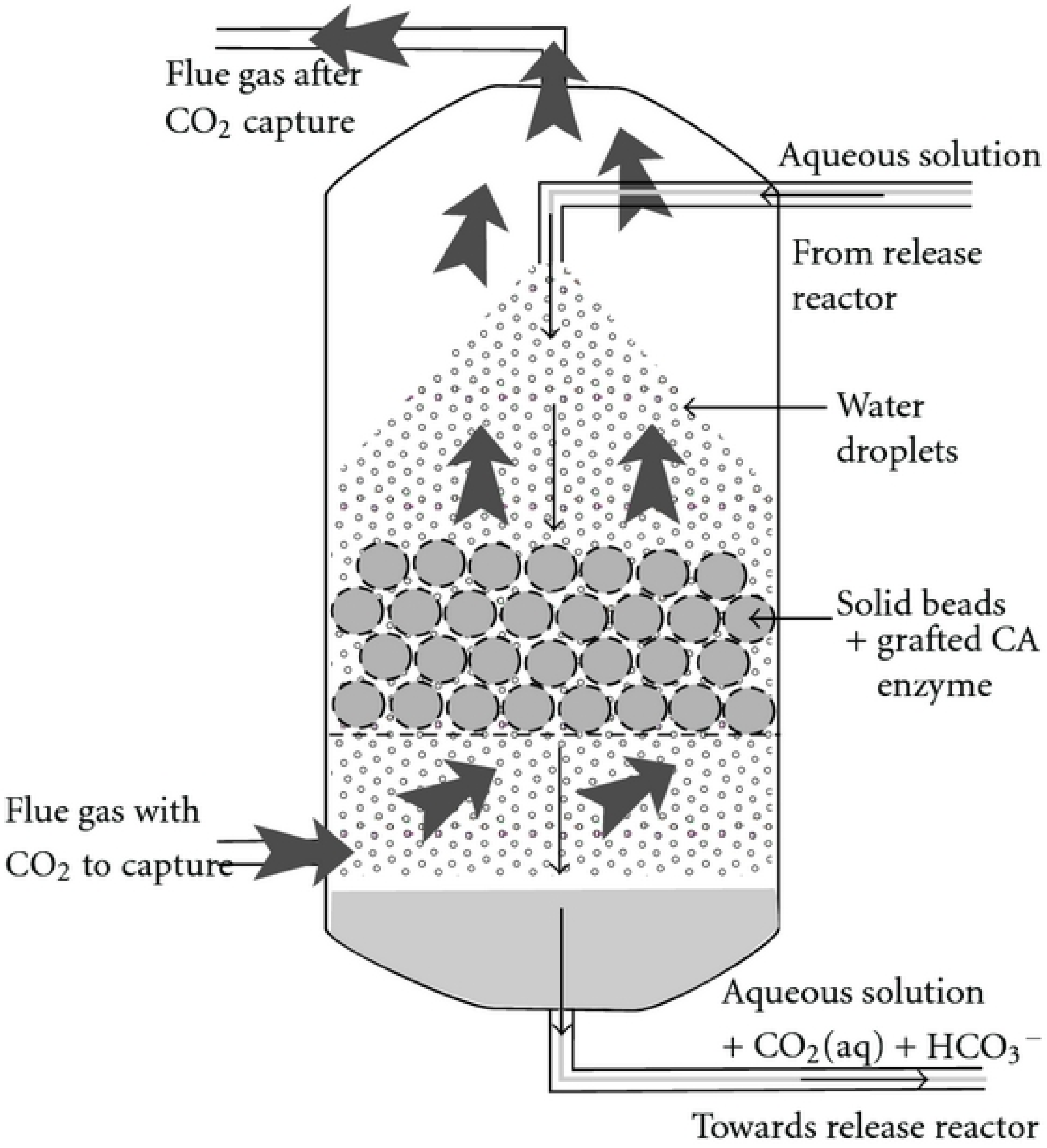


Seems like amine-absorption is “so ready” as a capture technology ☺

- I would like to quickly highlight one modification that is picking a lot of momentum within that domain.
- It is called “Enzyme catalyzed absorption”

Enzyme catalyzed absorption

- It is still amine-based chemical absorption process
- The only difference is that an enzyme (biocatalyst) immobilized on beads is placed in the absorber solvent → this expedites the hydration reaction (fast rate of hydrolysis of CO_2 dissolution) → most efficient capture



https://www.hindawi.com/journals/isrn/2012/753687/

Helpful Resources

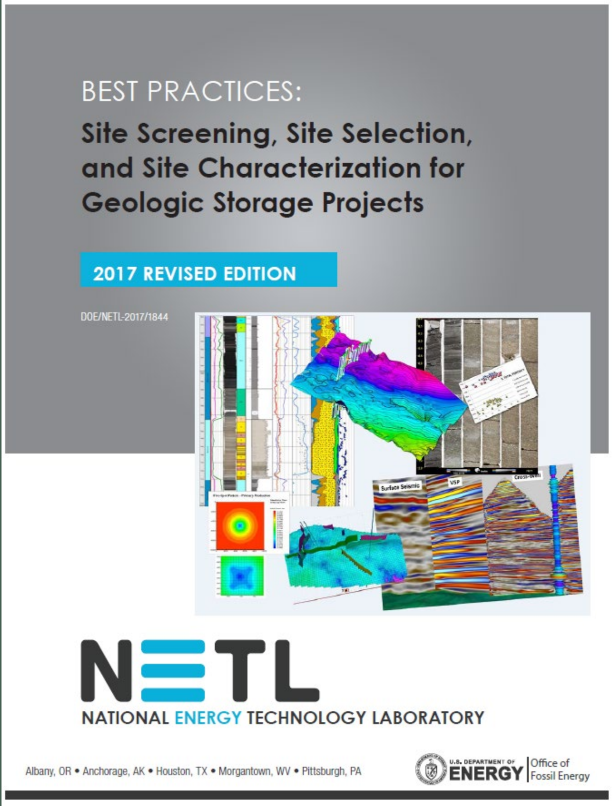
Department of Energy

The Department of Energy (DOE) has published a series of best practice manuals designed to share lessons learned through its regional carbon sequestration partnership activities as well as its research and development activities. The best practices were first published in 2011 and were updated in 2017 to incorporate lessons learned from the large-scale field projects conducted by the regional carbon sequestration partnerships.

The DOE Best Practice Manuals are:

- Monitoring, Verification, and Accounting (MVA) for Geologic Storage Projects[89]
- Public Outreach and Education for Geologic Storage Projects[90]
- Site Screening, Site Selection and Site Characterization for Geologic Storage Projects[91]
- Risk Management and Simulation for Geologic Storage Projects[92]
- Operations for Geologic Storage Projects[93]
- Geologic Formation Storage Classification[94]

The DOE has also established guidance, documentation templates, training resources, and a toolkit for CO_2 utilization LCA.[95]


BEST PRACTICES:
Site Screening, Site Selection, and Site Characterization for Geologic Storage Projects
2017 REVISED EDITION
DOE/NETL-2017/1844
NETL
NATIONAL ENERGY TECHNOLOGY LABORATORY
Albany, OR • Anchorage, AK • Houston, TX • Morgantown, WV • Pittsburgh, PA
U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy


BEST PRACTICES:
Operations for Geologic Storage Projects
2017 REVISED EDITION
DOE/NETL-2017/1848
NETL
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U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy


BEST PRACTICES:
Monitoring, Verification, and Accounting (MVA) for Geologic Storage Projects
2017 REVISED EDITION
DOE/NETL-2017/1847
NETL
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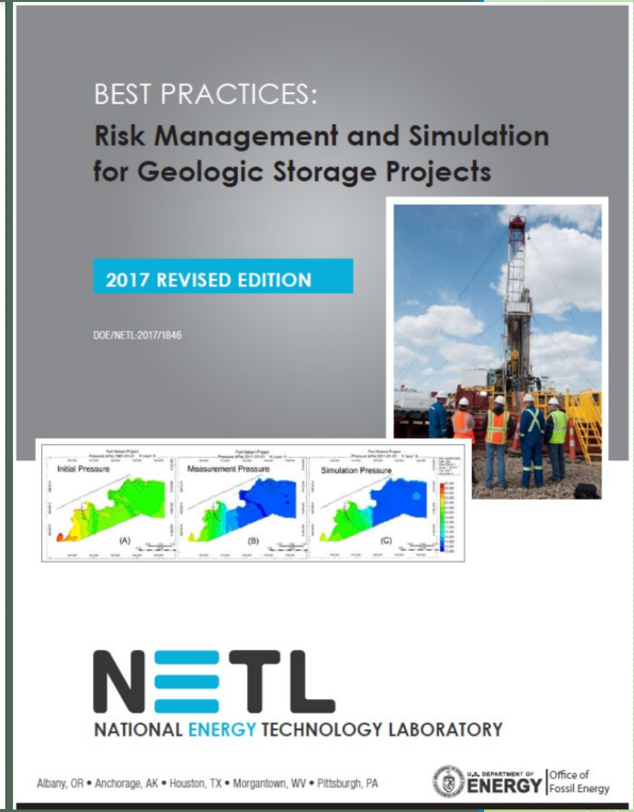
BEST PRACTICES:
Risk Management and Simulation for Geologic Storage Projects
2017 REVISED EDITION
DOE/NETL-2017/1846
Initial Pressure
Measurement Pressure
Simulation Pressure
NETL
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U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy

Environmental Protection Agency (EPA)

The EPA has published a series of guidance documents to support regulators and project developers in complying with the UIC program Class VI geologic sequestration regulations, including:

- Class VI Implementation Manual for UIC Program Directors[75]
- Class VI Well Plugging, Post Injection Site Care and Site Closure Guidance[76]
- Class VI Record-keeping, Reporting, and Data Management Guidance for Owners and Operators[77]
- Class VI Primacy Manual for State Directors[78]
- Class VI Well Site Characterization Guidance[79]
- Class VI Well Area of Review Evaluation and Corrective Action Guidance[80]
- Class VI Well Testing and Monitoring Guidance[81]
- Class VI Well Project Plan Development Guidance[82]
- Class VI Well Construction Guidance[83]
- Research and Analysis in Support of UIC Class VI Program Financial Responsibility Requirements and Guidance[84]
- Key Principles in EPA's UIC Program Class VI Rule Related to the Transition of Class II Enhanced Oil or Gas Recovery Wells to Class VI[85]

Council on Environmental Quality Report to Congress on Carbon Capture, Utilization, and Sequestration, 2021

Relevant API Specifications and Recommended Practices (RPs)

API Specification 5CT – Specification for Casing and Tubing

API RP 5C1 – Recommended Practices for Care and Use of Casing and Tubing

API RP 10B-2 – Recommended Practice for Testing Well Cements

API Specification 10A – Specification on Cements and Materials for Well Cementing

API RP 10D-2 – Recommended Practice for Centralizer Placement and Stop Collar Testing

API Specification 11D1 – Packers and Bridge Plugs

API RP 14B – Recommended Practice 14B, Design, Installation, Repair, and Operation of Subsurface Safety Valve Systems

API RP 14C – Recommended Practice 14C, Recommended Practice for Analysis, Design, Installation and Testing of Basic Surface Safety Systems for Offshore Production Platforms

API Guidance Document HF1 – Hydraulic Fracturing Operations - Well Construction and Integrity Guidelines

Figure 1. Relevant API Specifications and Recommended Practices (RP) for Injection Well Construction

Thank You!

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