Ocean & Geologic Sequestration of CO_2 with Particle Stabilized Emulsions for GHG Mitigation

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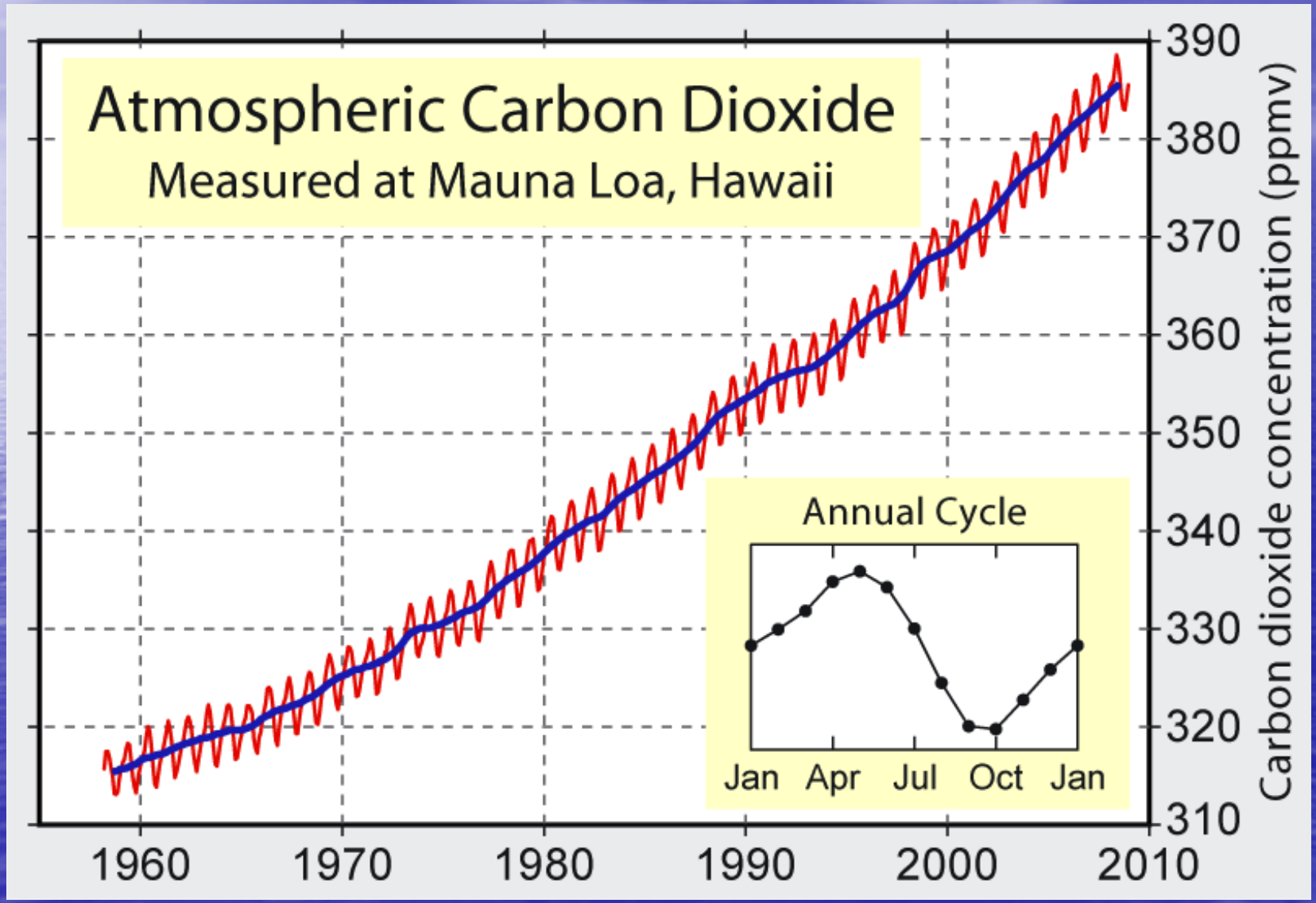
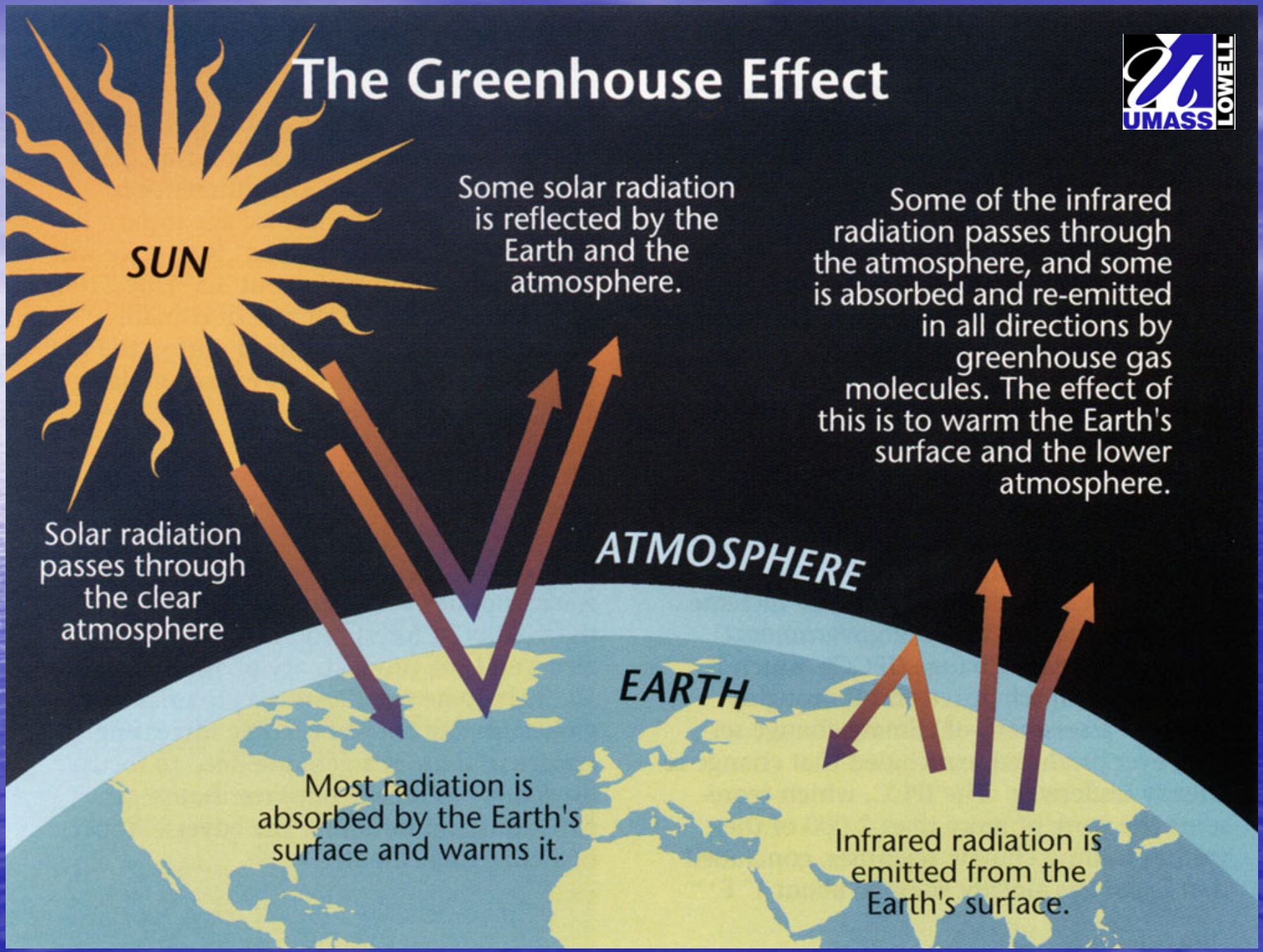
The Problem

Atmospheric CO_2 Levels on the Rise



Source: Keeling et al.



Source: OSTP (w/o greenhouse avg. earth temp. ~ -25°C instead of +15°C with)

The Answer

Or at least one answer

CO_2 Sequestration

- Storing or permanently immobilizing CO_2 in some form to remove it from the atmosphere or prevent it from entering the atmosphere
- General schemes include
  - Capture and store
    - In geologic formations
    - In the deep ocean
  - Converting to Biomass (terrestrial or oceanic e.g. IRONEX program for ocean fertilization)

CO_2 Emissions Can Be Reduced By Several Means (other answers)

- Conservation and efficiency improvements
- Substitute high carbon fuels (i.e. coal) with low carbon fuels (i.e. natural gas)
- Renewable energies
  1. Wind
  2. Solar (UMass Lowell Team – Solar Decathlon)
  3. Biomass
  4. Geothermal
  5. Ocean thermal, ocean tides, ocean waves
- Nuclear energy

CO_2 Emissions By Sector USA 2016

	Mt CO_2/y	%
Electric power plants	1821	26
Industrial	1388	20
Transportation	1883	27
Residential	998	14
Commercial	902	13
Total	6992	100

Source: U.S. Energy Information Administration, April 2017

Global Emissions of CO_2 for Large Stationary Sources

Process	No. of sources	Emissions ($MtCO_2/yr$)
Fossil Fuels		
Power (coal, gas, oil and others)	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	N/A	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91
Total	**7,887**	**13,466**

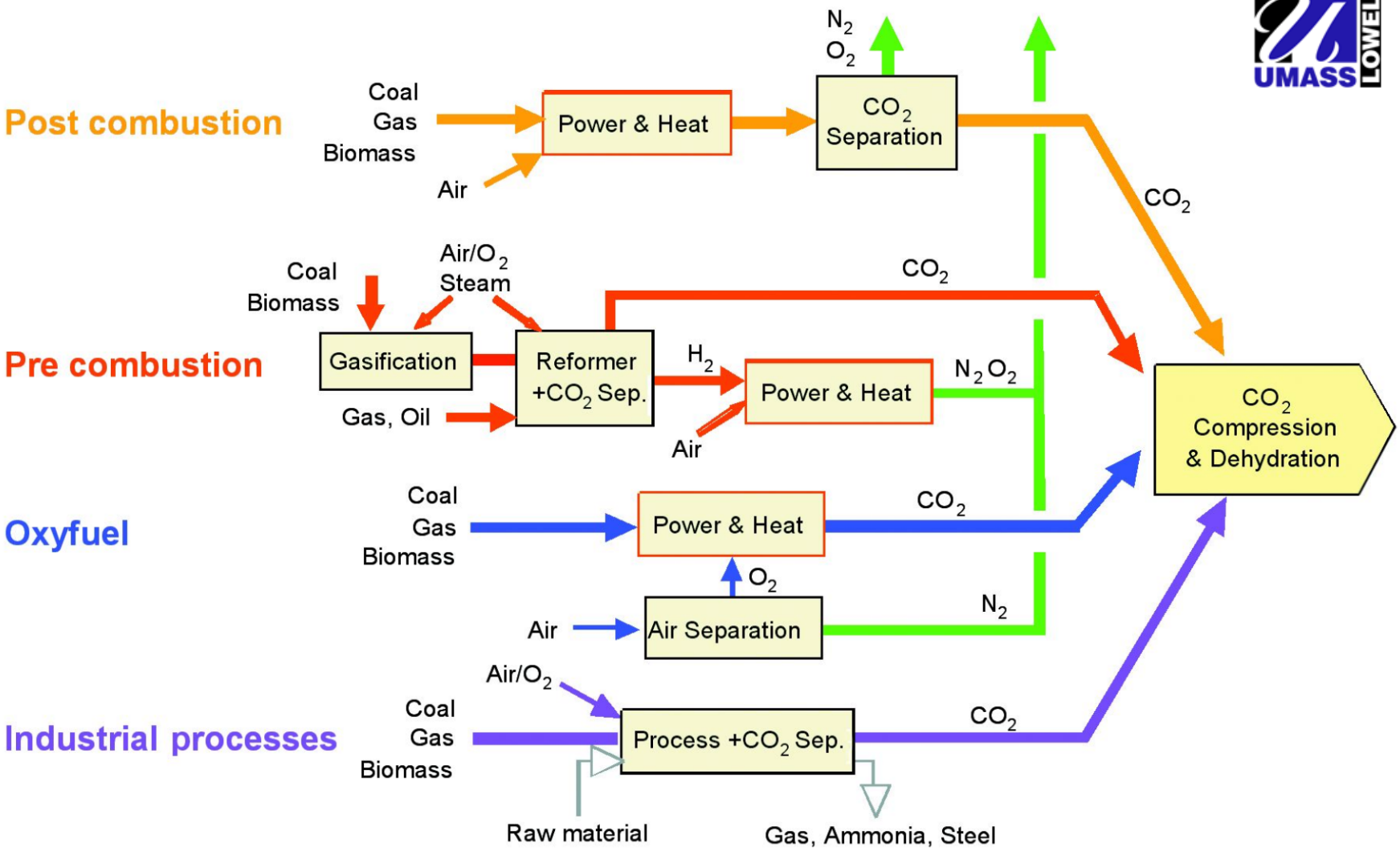
How it Works

CO_2 Capture Technologies

Ways of capturing CO_2 before it is released to the atmosphere:

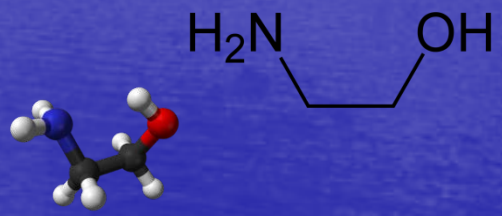
- Chemical absorption
- Physical adsorption
- Coal gasification with physical adsorption
- Oxyfuel combustion

Overview of CO_2 Capture Schemes



CO_2 Capture Technologies

Ways of capturing CO_2 before it is released to the atmosphere:



- Chemical absorption
- Physical adsorption
- Coal gasification with physical adsorption
- Oxyfuel combustion

$3C\ (i.e.,\ coal) + O_2 + H_2O \rightarrow H_2 + 3CO$

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + energy$

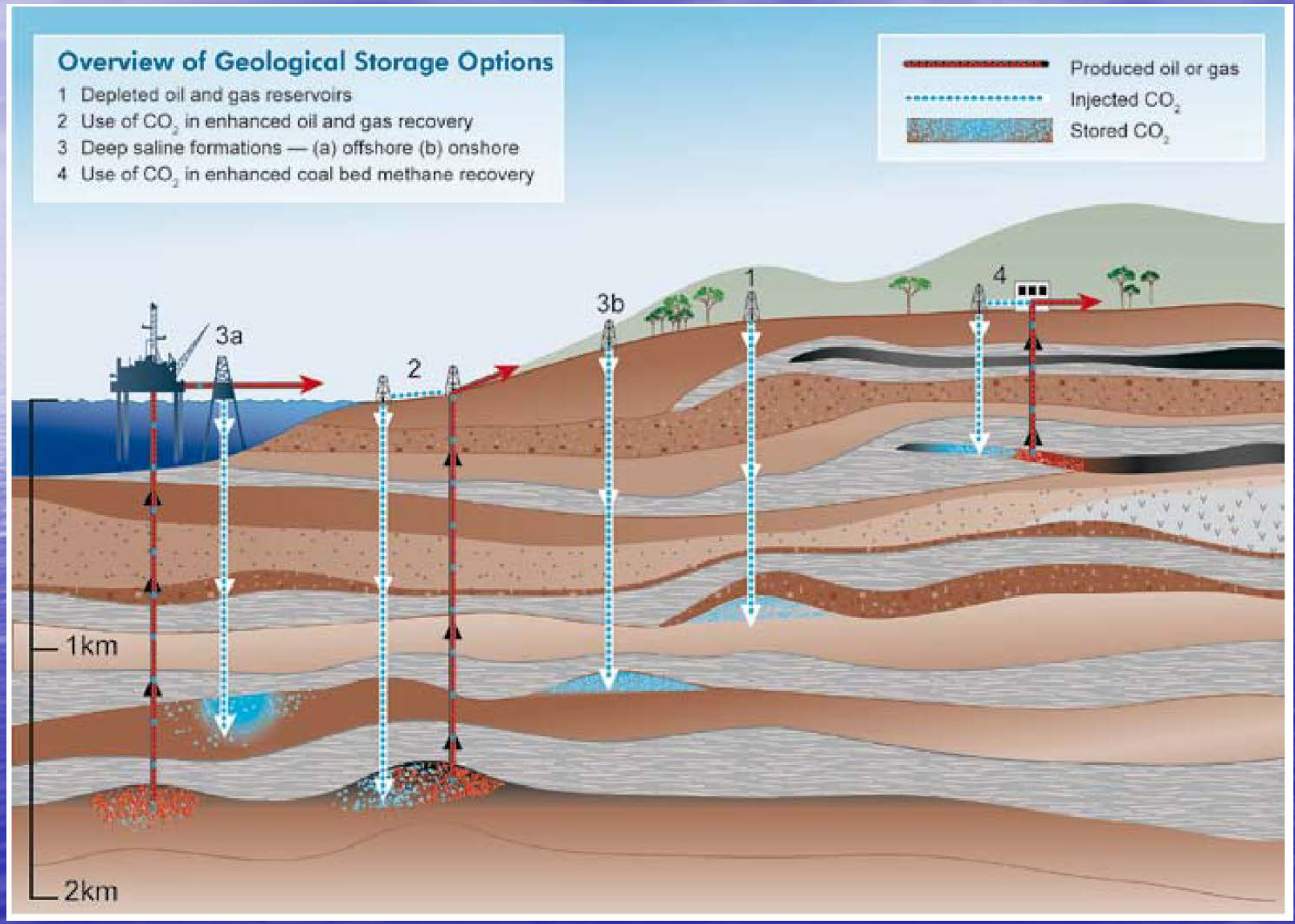
$CO + H_2O \rightarrow CO_2 + H_2$

$2\ H_2 + O_2 \rightarrow 2\ H_2O(g) + heat$

Then What ?

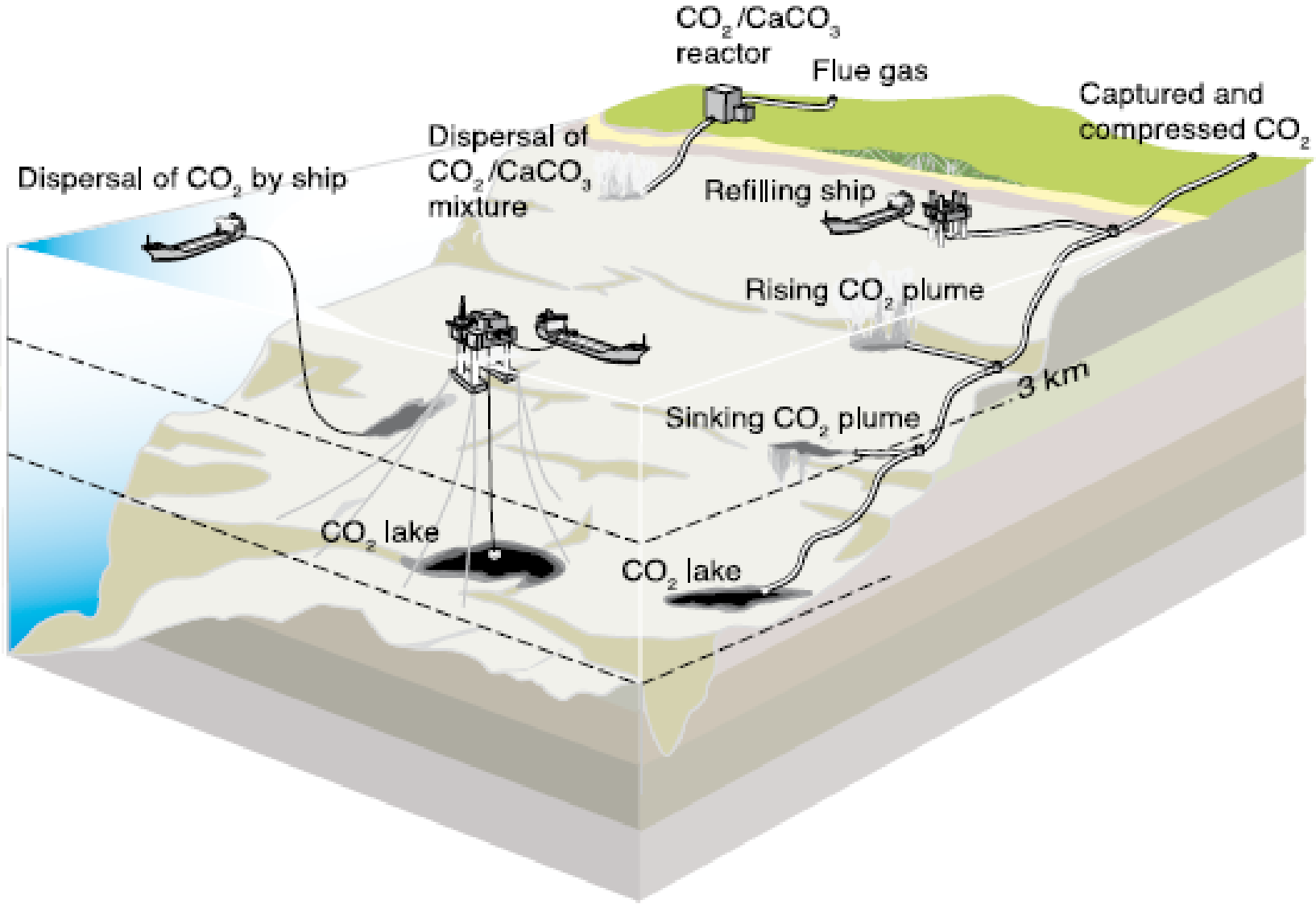
CO_2 Sequestration

Geologic Sequestration



Source: U.S. DOE

Ocean sequestration options



Source: IPCC Special Report on CC&S, 2005

Problems with Scenarios for Ocean Sequestration of CO_2

- High Costs - exclusive of capture
- Proximity of Sources to Ocean
- Ecological Effects
  - Physical Impact of Immiscible Liquid
  - Chemical Impacts
    - pH
    - Carbonate hot spots
- Long Term Uncertainty
  - Chemical Effects
  - Lake Nyos Syndrome
- London Convention 1972

Our Discovery

In 2001 we discovered how to make emulsions of liquid CO_2 and water stabilized by fine particles

Some simple chemistry

- Immiscible liquids form two layers with an **interfacial tension** or force between them

Applying shear force or mixing creates a dispersion

Droplets of a dispersion quickly coalesce to larger & larger drops resulting in two layers once again

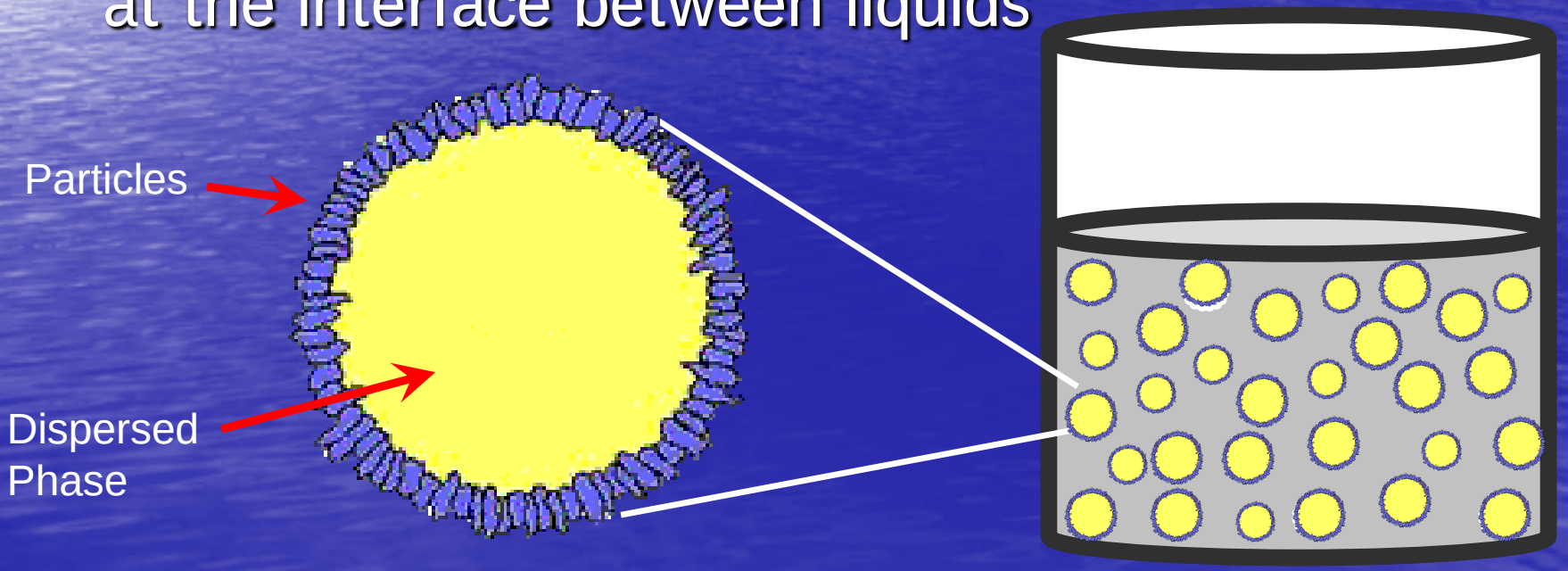
Emulsions

- When an **emulsifying agent** is added to a two phase system, interfacial tension is greatly reduced allowing formation of stable dispersions or emulsions

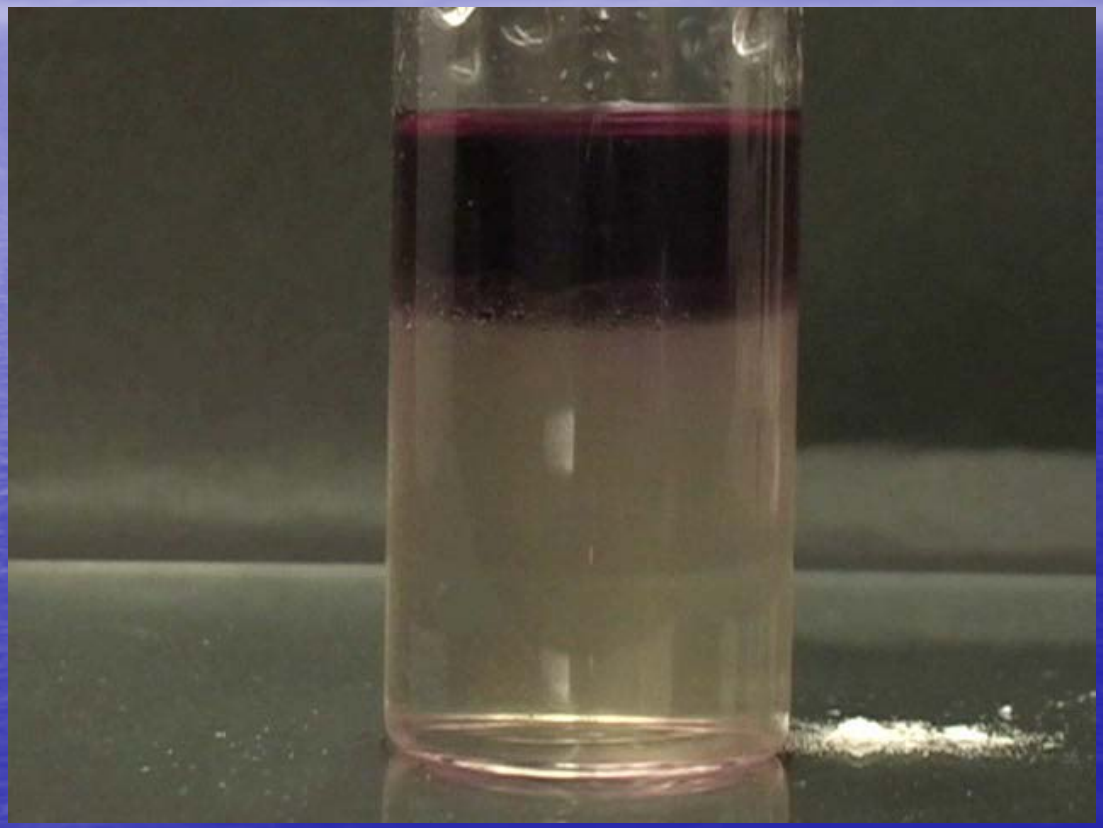
- Emulsions can be either **macroemulsions** or **microemulsions** depending on droplet size

Particle Stabilized Emulsions (also called Pickering Emulsions)

- Very fine particles can act as emulsifying agents, though more common emulsifiers are surfactants like soaps and detergents
- Emulsifying agents work by arranging themselves at the interface between liquids



Particle Stabilized Emulsions



Immiscible liquids form an emulsion with fine particles

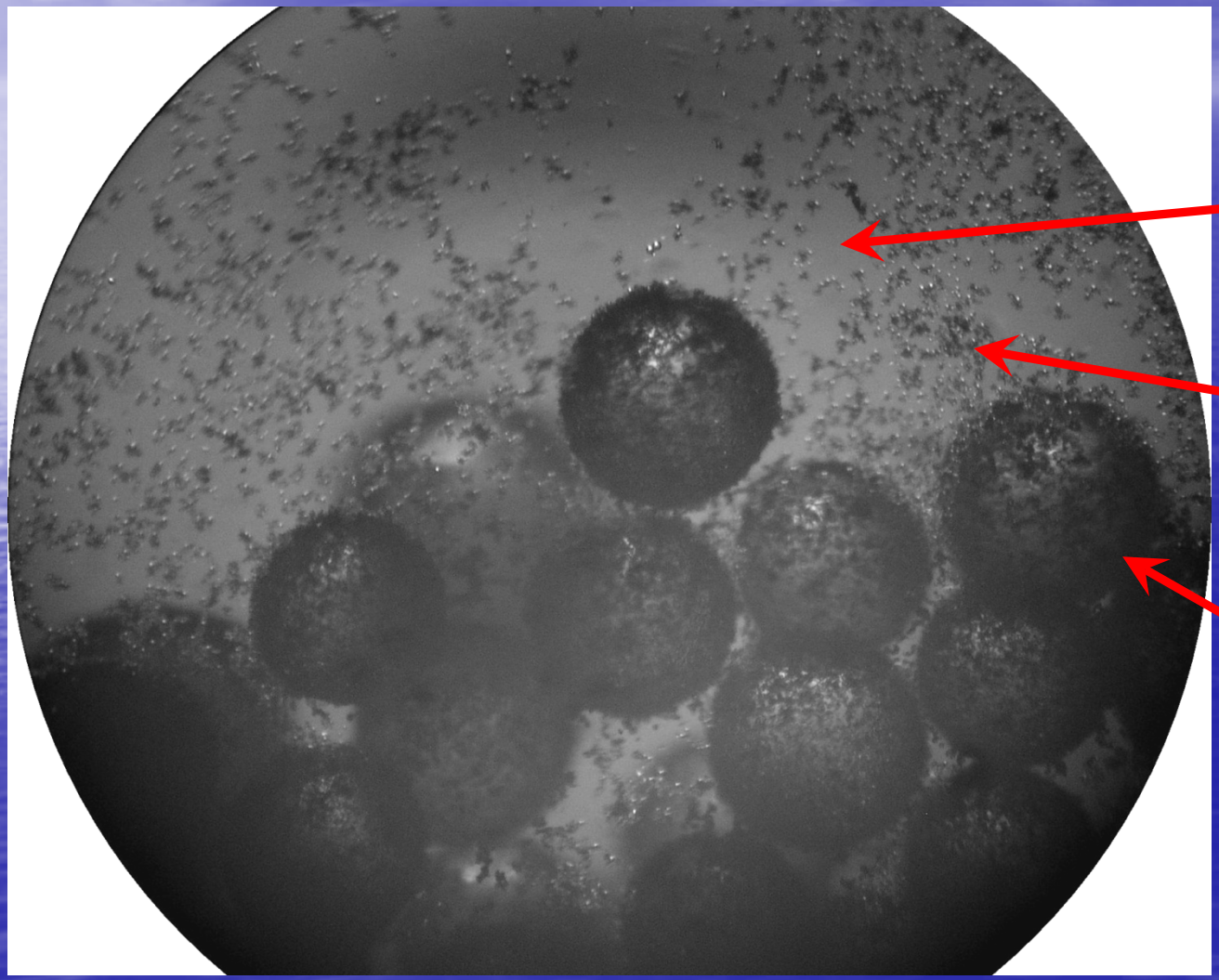
System: dodecane (top), water, calcite and iodine for color

Particle Stabilized Emulsions

- **Hydrophilic particles** form oil-in-water emulsions:
  - Calcite ($CaCO_3$)
  - Pulverized sand (SiO_2)
  - Lizardite & other minerals

- **Hydrophobic particles** form water-in-oil emulsions:
  - Carbon black
  - Pulverized coal
  - Teflon particles

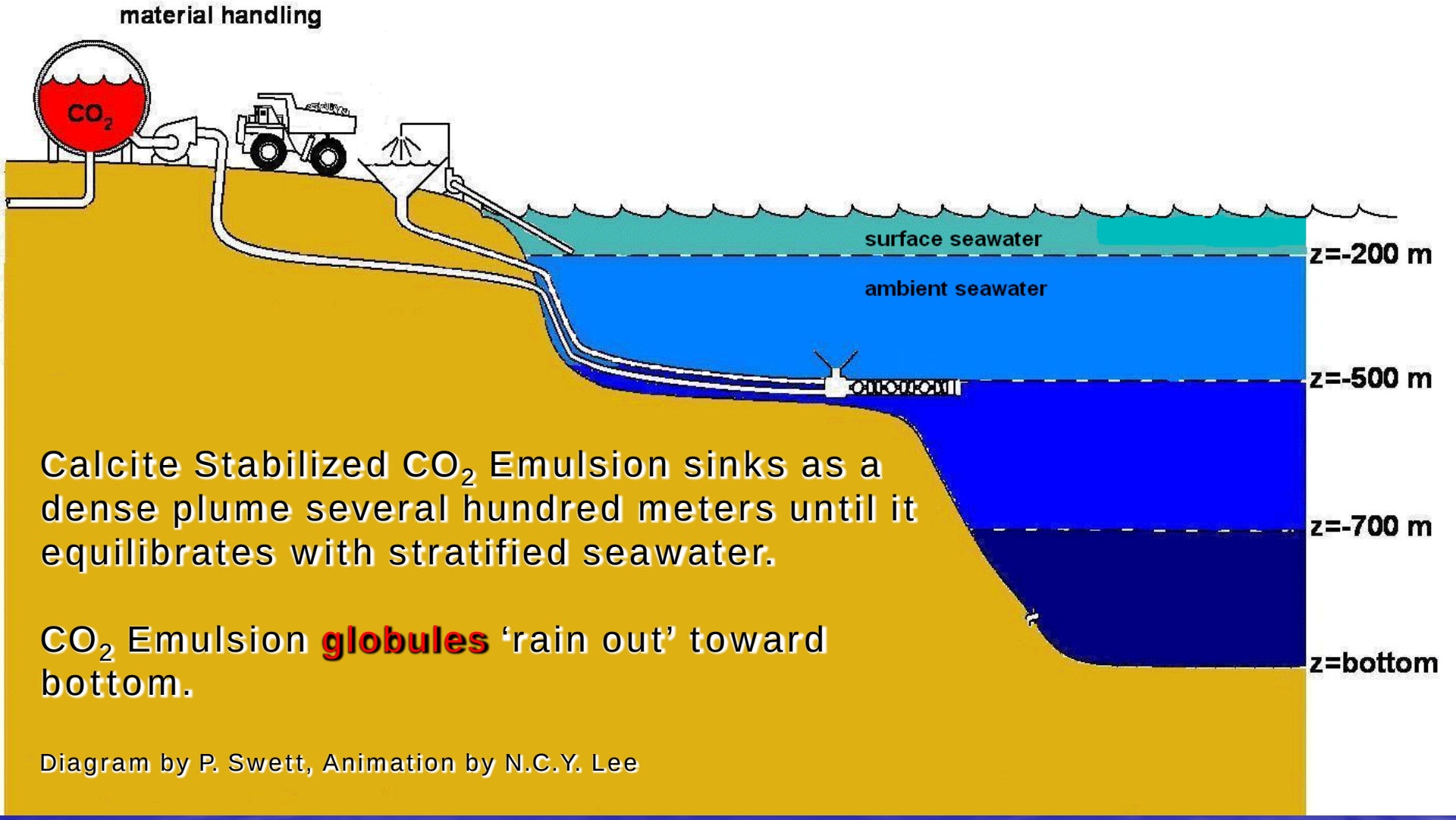
Liquid CO_2/Seawater/$CaCO_3$ Macroemulsion (a.k.a. Globulsion)



~200 µm droplets (globules)

The Grand Finale

Ocean Sequestration Scenario



Calcite Stabilized CO_2 Emulsion sinks as a dense plume several hundred meters until it equilibrates with stratified seawater.

CO_2 Emulsion **globules** 'rain out' toward bottom.

Diagram by P. Swett, Animation by N.C.Y. Lee

Environ. Sci. Technol. **2007**, *41*, 4698–4704

Ocean Sequestration of Carbon Dioxide: Modeling the Deep Ocean Release of a Dense Emulsion of Liquid CO_2-in-Water Stabilized by Pulverized Limestone Particles

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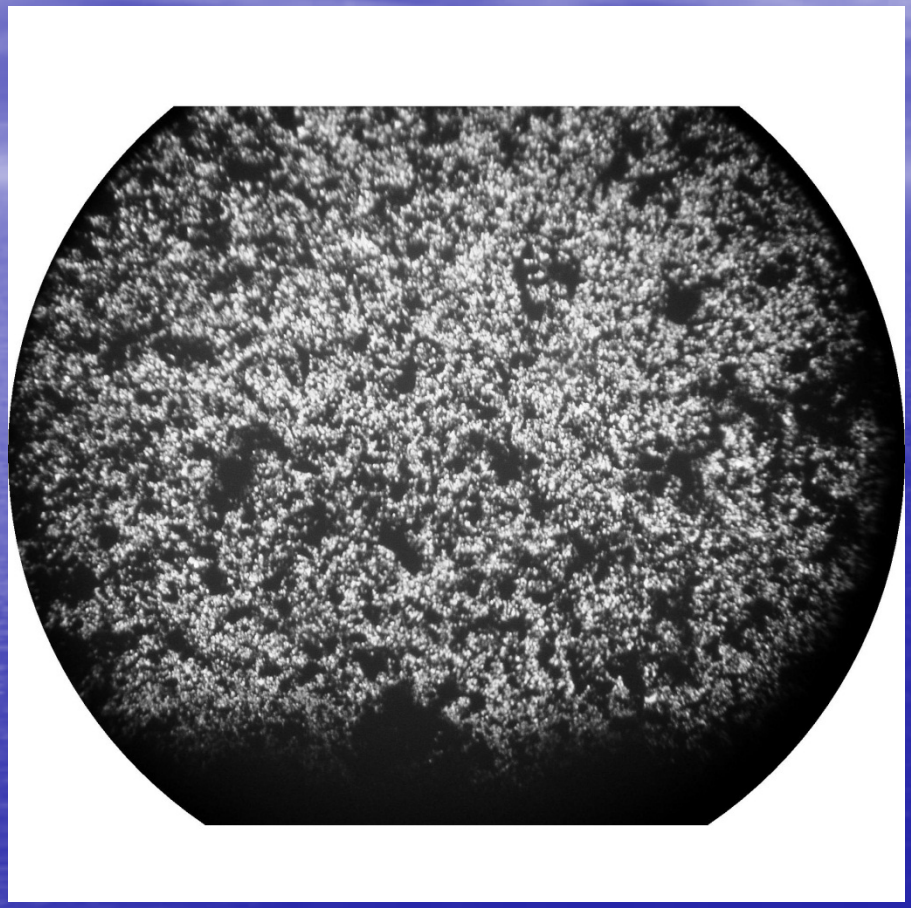
See also ***Environ. Sci. Technol.*** **2004, *38*, 4445-4450**
Ind. Eng. Chem. Res. **2006, *45*, 2728-2733**

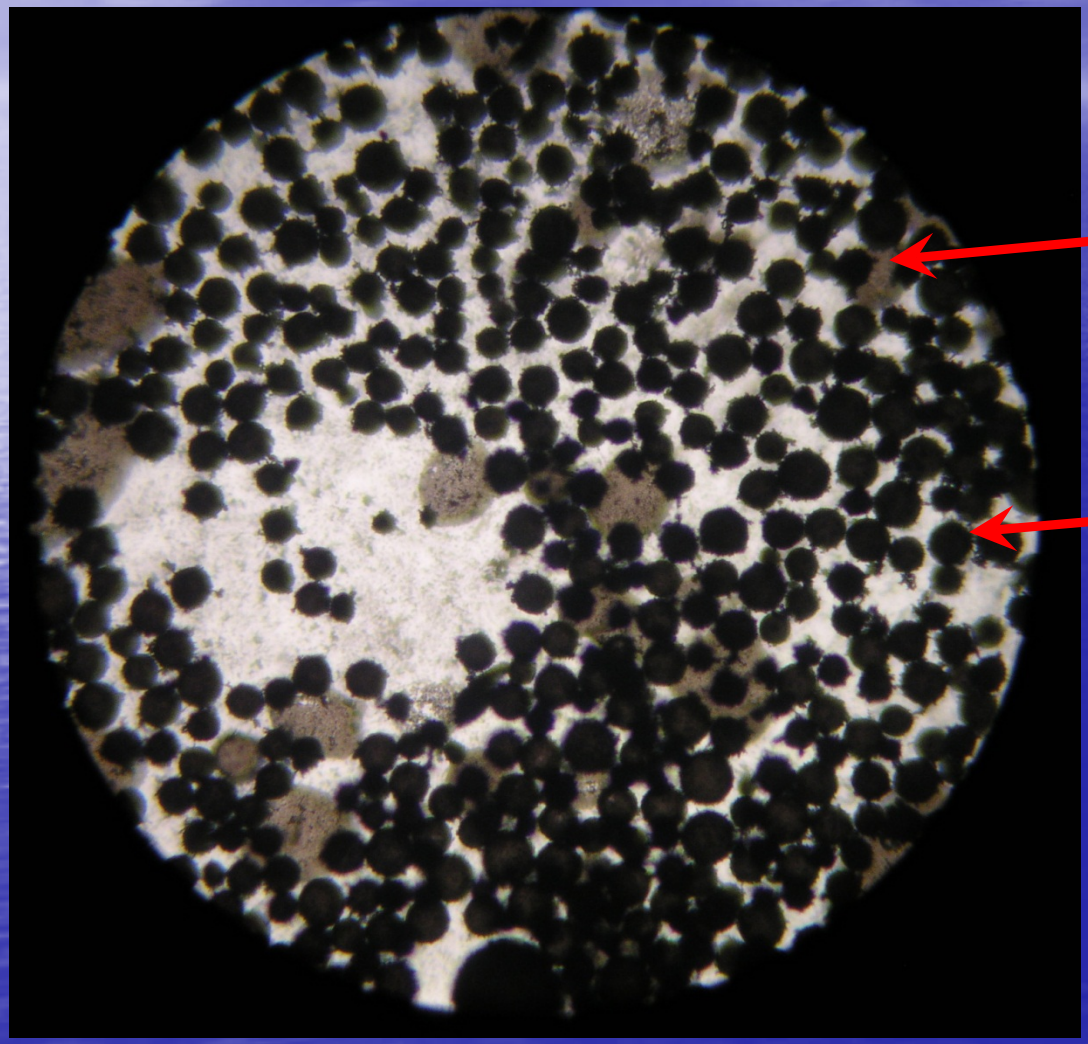
What Next ?

Inverted Emulsions



Water-in-Liquid CO_2 (W/C) emulsion stabilized by pulverized coal particles. 70% CO_2(*l*)/30% H_2O(*l*), 2% pulverized coal, 4 μm mean particle diameter.

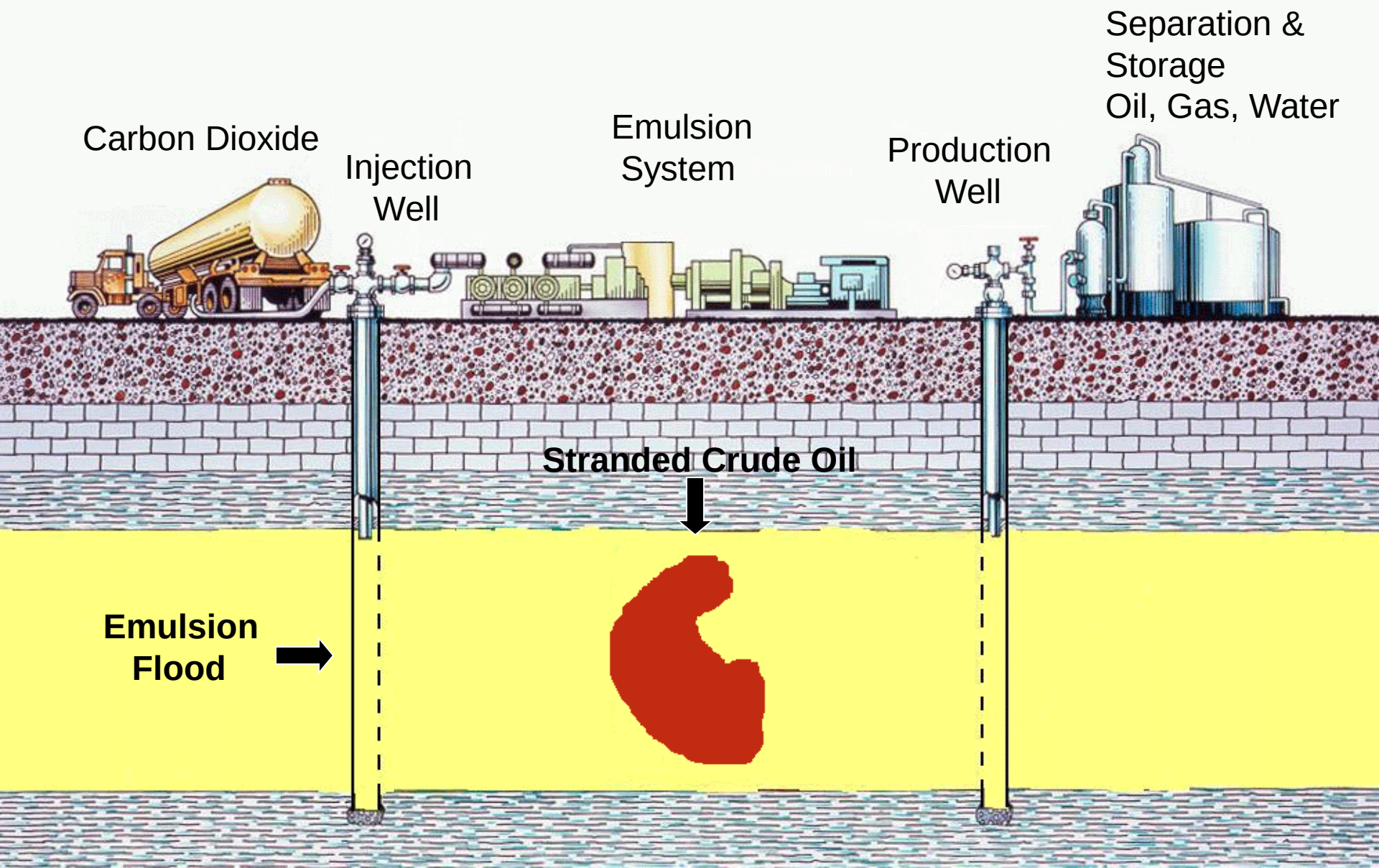
Dodecane/Water/Carbon Black Microemulsion (10-20 μm) for EOR



Dodecane

Carbon Black Coated Water Droplets

EOR with Particle Stabilized Emulsions of CO_2 & Water

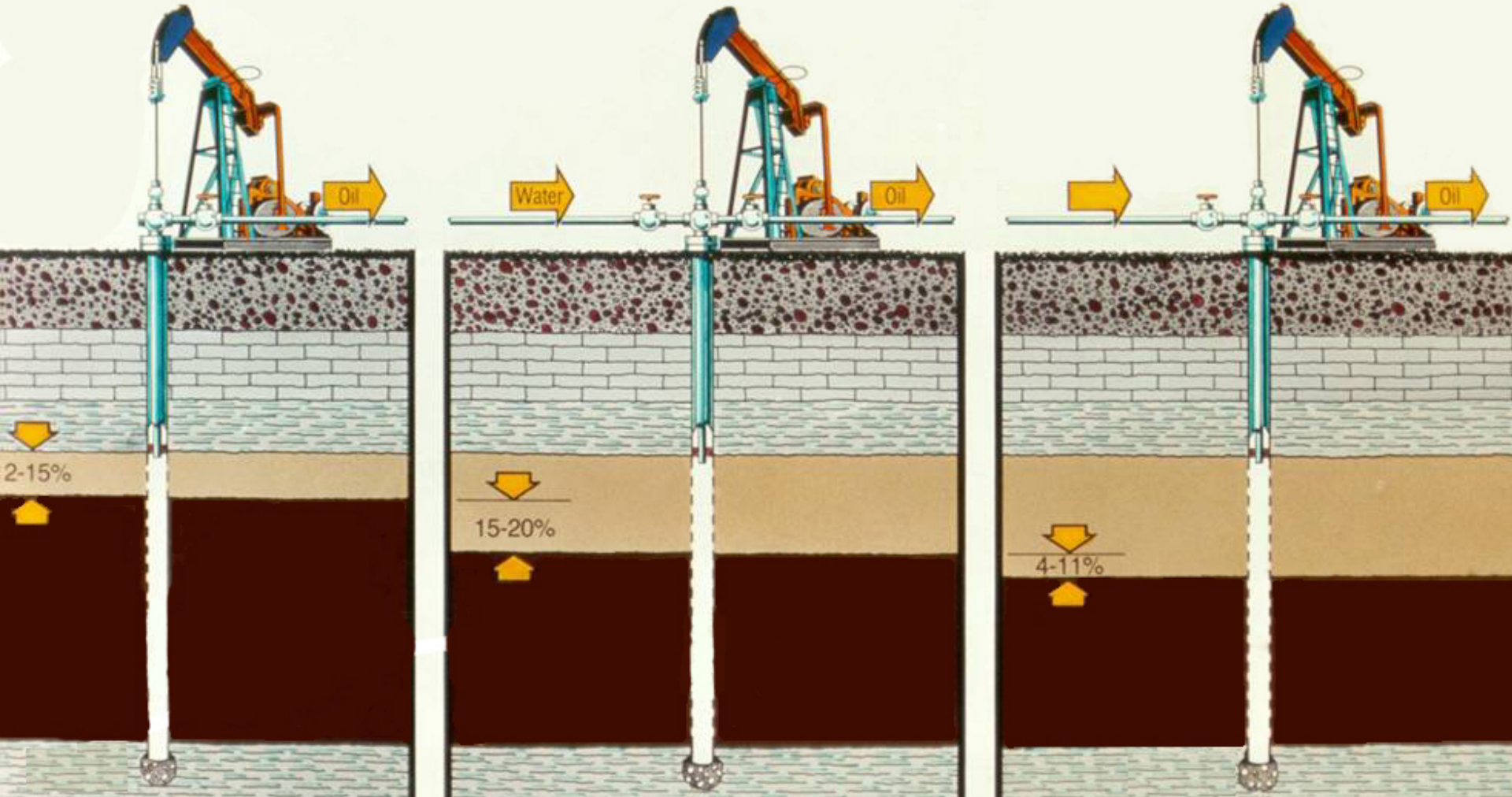


Production

Primary
Simple Pumping

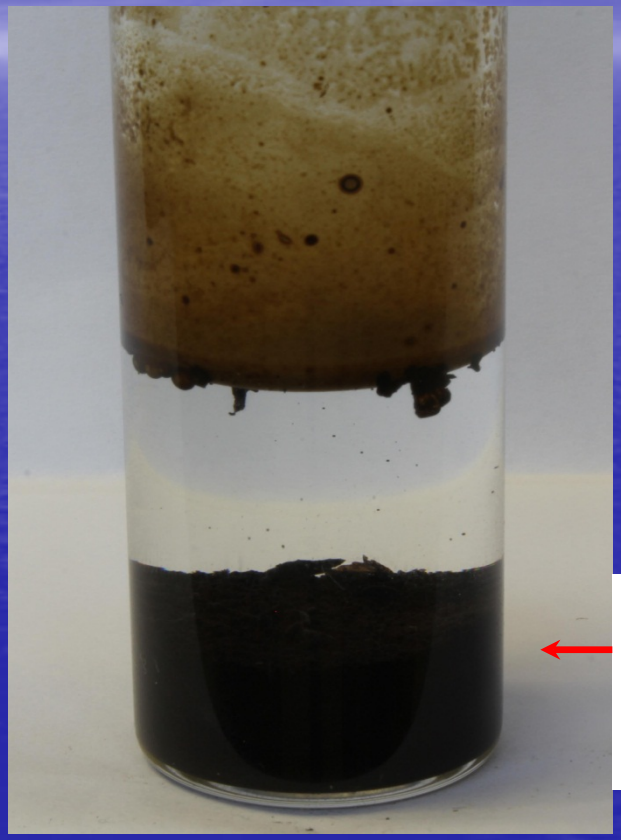
Secondary
Water Flooding

Tertiary
EOR



Sinking Crude Oil Emulsion

Before Emulsion Formation
Crude Oil on Seawater



Dense Crude Oil Emulsion
with Calcite