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CEE 697z
Organic Compounds in Water and Wastewater

Hydraulic Fracturing
Adverse Environmental Impacts

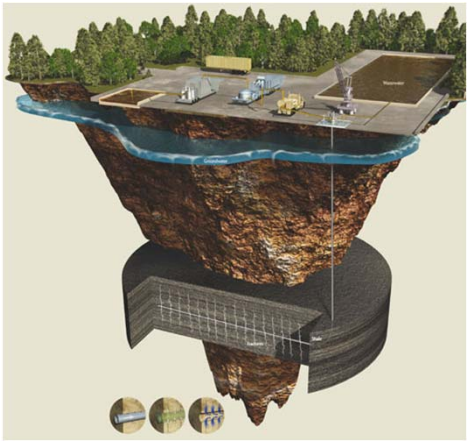
Rassil El Sayess: Lecture #12

Introduction

- In nature, geologic formations may contain pockets of large quantities of oil or gas
  - Poor flow rate due to low permeability
  - Tight sands, shale, coal bed methane formations

Geology of fracturing site

- At the fracturing drill site, the geology is as follows:
  - Soil at the top
  - An aquifer about 50-800 ft below the soil
  - About 5000 ft of limestone/sandstone below that
  - Shale 6000 -8000 ft below surface



Hydraulic fracturing (Fracking)

- Process of trying to simulate the environment
- A well is drilled and steel pipe (casing) inserted into the well bore
- Fracking fluid (water + sand (99.5%) and chemicals) is then injected under high pressure into the shale rock layer deep underground
- When the target formation cannot absorb the fluid as quickly as it's being injected, creates "fractures" in the shale
- Hydrocarbons (like gas and oil) contained inside seep out
- A propping agent is pumped into the fractures to keep them from closing when the pumping pressure is released
- 25-50% of fracking fluids are recovered to the surface (flowback) and wastes are stored in open pits or tanks at the well site prior to disposal

Process of Simulating the Environment

- https://www.youtube.com/watch?v=fFUxq9UolN4

Fracking fluid

- 8 million gallons injected into the shale, under high pressure
- Due to extreme pressure and corrosiveness, toxic fluid expands fractures in shale
- Chemicals in fracking fluid (http://fracfocus.org/chemical-use/what-chemicals-are-used)
- Fracking fluid is retrieved from the shale ("flowback")
  - 25-50% only
  - Stored in lined pits
  - Poor lining allows pits to leak

Sources of contamination

- Neglected surface pumps
- Unlined storage pits
- New fractures release methane
- Insufficient or improper casings

Improper/Insufficient Casing

- Manganese
- Bis(2-ethylhexvl)phthalate
- Barium sulfate
- Arsenic
- Glycol compounds
- Methane

- Leads to fracking fluid leaks
- Fugitive methane leaks along a wall
- Low quality concrete allows fugitive methane to rise
- Fugitive methane in casings, follows path to aquifer
- Residential wells pump contaminated water into house
- Dissolved methane enters residence

Why are chemicals added?

Additive	Purpose
Acid	Helps dissolve minerals and initiate cracks in the rock
Acid/Corrosion Inhibitor	Protects casing from corrosion
Biocide	Eliminates bacteria in the water that can cause corrosive by products
Base Carrier Fluid (water)	Create Fracture Geometry and Suspend Proppant
Breaker	Allows a delayed break down of gels when required.
Clay and Shale Stabilization/control	Temporary or Permanent Clay Stabilizer to lock down clays in the shale structure
Crosslinker	Maintains viscosity as temperature increases
Friction Reducer	Reduces Friction effects over base water in pipe
Gel	Thickens the water in order to suspend the proppant
Iron Control	Iron chelating agent that helps prevent precipitation of metal oxides
Non-Emulsifier	Used to break or separate oil / water mixtures (emulsions)
pH Adjusting Agent/Buffer	maintins the effectiveness of other additives such as crosslinkers
Propping Agent	Keeps Fractures Open allowing for hydrocarbon production
Scale Inhibitor	Prevent Scale in Pipe and Formation
Surfactant	Reduces the surface tension of the treatment fluid in the formation and helps improve fluid recovery from the well after the frac is completed

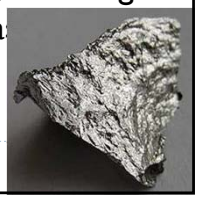
Fracfocus, a chemical disclosure registry http://fracfocus.org/chemical-use/why-chemicals-are-used

Fracking fluid

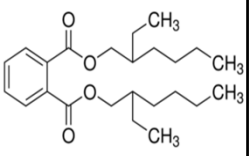
- Manganese
- Bis(2-ethylhexyl)phthalate
- Barium sulfate
- Arsenic
- Glycol compounds (e.g., ethylene glycol)
- Methane

Manganese (Mn^0,MW=54.98 g/mol)

- Manganese is a mineral that is found in several foods including nuts, legumes, seeds, tea, whole grains, and leafy green vegetables
- Considered an essential nutrient, because the body requires it to function properly. People use manganese as medicine.
- Manganese is likely safe for most adults in amounts up to 11 mg per day.
- Excess manganese can cause serious side effects, including symptoms resembling Parkinson's disease, such a (tremors).

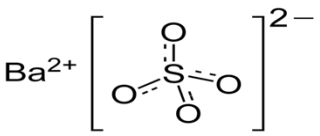


Bis(2-ethylhexyl) phthalate (DEHP) (MW=390.56 g/mol)



- Widely used as a plasticizer in manufacturing of articles made of PVC
- Hydrolyzes to mono-ethylhexyl phthalate (MEHP) and subsequently to phthalate salts.The released alcohol is susceptible to oxidation to the aldehyde and carboxylic acid
- Toxicity: potential as an endocrine disruptor
- Developmental problems on fetuses of pregnant women
- American men with abdominal obesity or insulin resistance (a precursor to diabetes) were more likely to have high levels of [DEHP and dibuytl phthalate] metabolites in their urine than men without those problems
- A clinically relevant dose and duration of exposure to DEHP shown to have a significant impact on the behavior of cardiac cells in culture

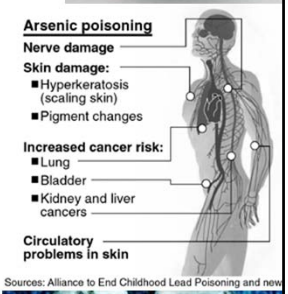
Barium Sulfate (BaSO4, 233.43 g/mol)

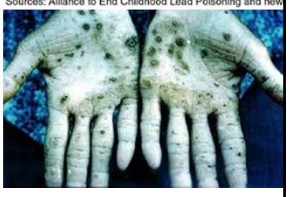


- It is a white crystalline solid that is odo and insoluble (not toxic) in water.
- Barium poisoning arises from the consumption of soluble barium salts mislabeled as $BaSO_4$
- About 80% of the world's barium sulfate production, is consumed as a component of oil well drilling fluid to increase the density of the fluid
- OSHA set a PEL at 15 mg/m^3 while the NIOSH has a recommended exposure limit at 10 mg/m^3.

Arsenic (As^0, 74.92 g/mol)

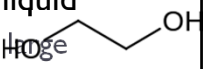
- If a large amount of arsenic is swallowed by humans, in a form that is readily absorbed, it can cause rapid poisoning and death.
- The gut, the heart and the nervous system are affected.
- Those who survive acute poisoning may develop pigment spots in the skin and damage to red blood cells, bone marrow (where blood cells are made), liver, nerves and brain.



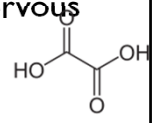


Ethylene glycol ($C_2H_6O_2$, 62.07 g/mol)

- It is an odorless, colorless, syrupy, sweet-tasting liquid
  - Children and animals are more inclined to consume large quantities of it



- Upon ingestion, is oxidized to glycolic acid which is, in turn, oxidized to oxalic acid, which is toxic.
- It and its toxic byproducts first affect the central nervous system, then the heart, and finally the kidneys
- Oral LD_{Lo} = 786 mg/kg for humans



Methane (CH4, 16.04 g/mol)

- Is extremely flammable and may form explosive mixtures with air.
- Is violently reactive with oxidizers, halogen, and some halogen-containing compounds.
- Is also an asphyxiant and may displace oxygen in an enclosed space.
  - If the oxygen concentration is reduced to below about 16% by displacement
  - Most people can tolerate a reduction from 21% to 16% without ill effects.

Some Additional Environmental Issues

Water Demand

- EPA estimates 70 to 140 billion gallons of water used to fracture 350 wells in the US every year== consumption of 40-80 cities with population of 50,000
  - Coalbed methane wells: 50,000 to 350,000 gallons of water per well
  - Deeper horizontal shale wells: 2 to 10 million gallons of water per well
- Most water used comes from surface water sources (lakes, rivers and municipal supplies). Groundwater can be used to augment surface water supplies.

Flowback Treatment

- Surface water discharges of the flowback are regulated by the National Pollutant Discharge Elimination System (NPDES) program
  - Flowback treated prior to discharge into surface water or underground injection prior to discharge
    - Typically performed by wastewater treatment facilities.
  - Underground injection of flowback is regulated by either EPA Underground Injection Control (UIC) program or a state with primary UIC enforcement authority.

- To next lecture