A Review of the Chemical Characteristics of Frac/Flowback/Produced Water

Workshop on Water Management in Marcellus Shale Gas Exploration and Production

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Summary

- Introduction and Definitions
- Gas Transmission
- Gas Production
- Produced Water Constituents
- Shale Gas and Hydrofracing
- Water Sources and Concerns
- Wastewater Issues
- Disposal Options of Produced Water/Flowback Water
- Applicable Regulations
- Conclusions

Introduction and Definitions

- Oil and gas exploration always associated with production of water
- Produced water contains contaminants from underground rock structures and chemical additives
- Due to rising oil prices, natural gas emerging as a major source of energy worldwide
- Many large reserves were untapped as gas is trapped within shale rock structures
- Gas produced from these structures called Shale Gas
- Now possible to tap those reserves with advanced technology (horizontal drilling and fracing)

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Introduction and Definitions

- Releasing shale gas during production requires fracturing the rock structures that trap the gas
- "Frac water" consists of water, sand (or another "proppant") and a small quantity of chemicals (anti-scalants, friction reducers and biocides), injected under high pressure. Rock is fractured at 1,500 to 6,000 meters depth.
- Frac water that returns during fracing (5-20%) is called flowback water. Flowback water contains dissolved solids from the reservoir and chemicals used in fracing.
- "Produced water" is water from the reservoir that flows to the surface with gas during the life of the well.

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Typical Raw Gas Composition

- Typical composition of Natural Gas:
  - CH_4 = 65 – 90%
  - C_2, C_3 and C_4 = Each ~ 1 - 15%
  - CO_2 = 1 - 5% (v/v)
  - H_2S and N_2 = 0.2 – 5,000 ppm (v/v)
  - Water = 3,500 – 5,000 kg/10^6 std m^3
  - Condensate = 4,500 – 6,000 kg/10^6 std m^3
  - Condensate is comprised of heavy hydrocarbon molecules and various other organic components
  - Heating Value ~ 9,000 kCal/std cu.m

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Issues in Gas Transmission

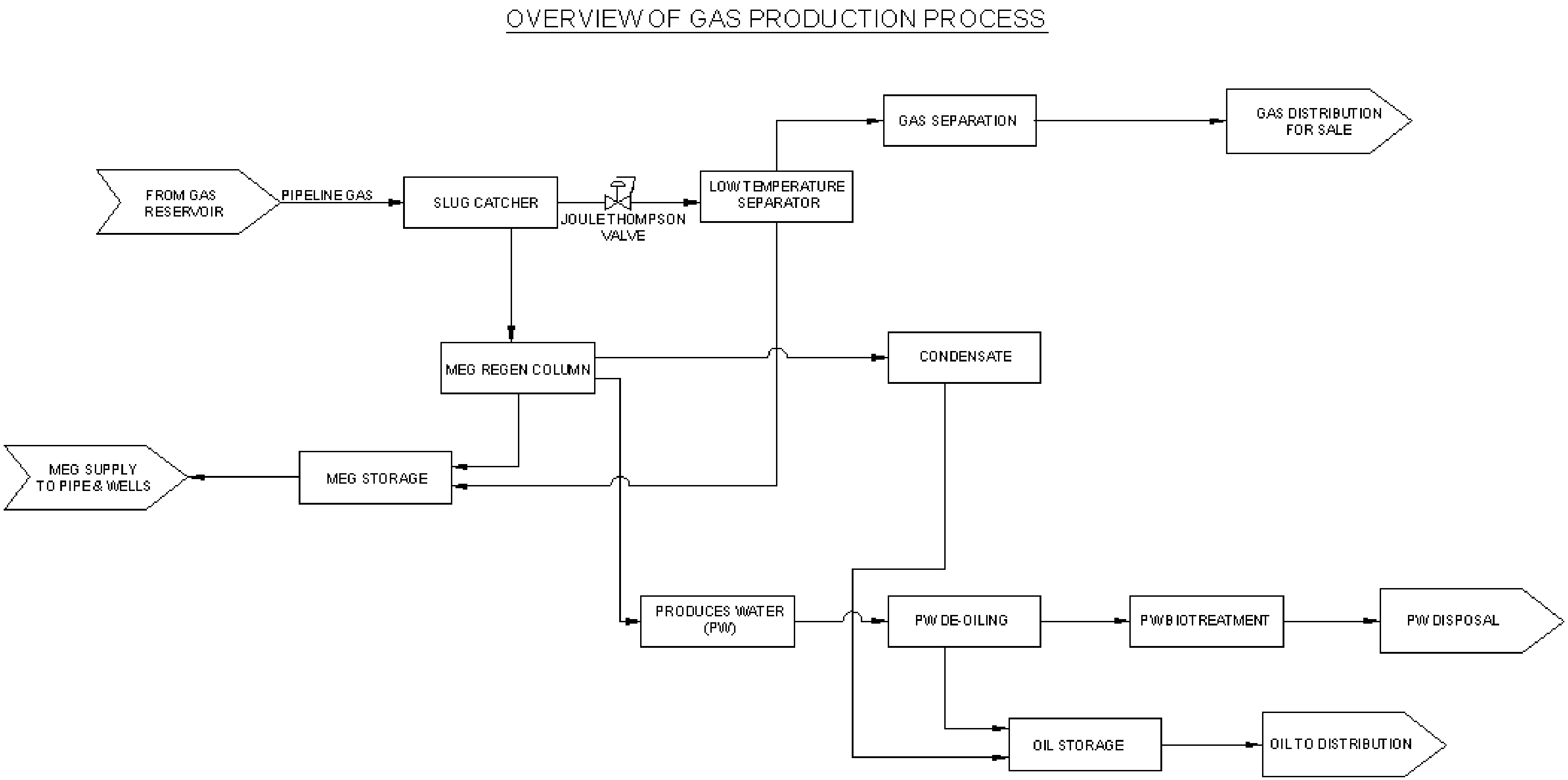
- Gas is released from the wells at pressures ~ 450 to 550 barg (Note: barg stands for bar gage)
- High pressure, associated with low temperature (particularly in offshore gas fields), causes formation of slugs of gas hydrate in the line
- Gas hydrate slugs are gas bubbles trapped within crystals of ice
- Slugs deposit on the internal surfaces of transmission pipes and cause obstruction to gas flow
- Monoethylene glycol (MEG) and methanol dosed in the well and pipes to prevent slugging in the pipe
- Pressure drops to ~ 30 to 50 barg during transmission

Properties of MEG ($OH-CH_2-CH_2-OH$)

- MEG performs as hydrate inhibitor

- Advantages of MEG
  - Depresses freezing point of water by affecting its hydrogen bonding
  - Low vapor pressure and low loss
  - Low toxicity
  - Not inflammable
  - Inexpensive
  - Regenerated and recycled in the gas processing facility
- Disadvantages of MEG
  - Moderately toxic
  - Lost in condensate and water in soluble form
  - Regenerated MED contamination by condensate
  - Formation of carbonate particles that need removal
  - Formation of iron sulfide that need removal
  - Lighter hydrocarbons trapped in MEG
  - MEG and methanol are dissolved and carried over to produced water
  - Recent research shows MEG promotes scaling by accelerating nucleation of barite (barium sulfate)

Overview of Gas Production Process



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Produced Water Constituents

- Contains both organic and inorganic constituents
- Organic constituents
  - Heavy hydrocarbon and high molecular weight organic acids, both free phase and emulsified
  - Dissolved light gases
  - Additives and treating chemicals
    - Anti-scaling agents
      - Various organic phosphonates (proprietary chemical)
      - Polyacrylates (propreitary chemical)
      - Phosphinopolycarboxylates (proprietary chemical)
    - Hydrate inhibitors
      - MEG
      - Methanol
  - All organic constituents are lumped together as TOC
  - Typical TOC range 100 to 2,000 mg/L depending upon location
  - At the same facility methanol alone in produced water can shoot up to a concentration of 5% occasionally with the release of slugs

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Produced Water Constituents

- Inorganic constituents
  - Salt in high concentrations (can be up to 250,000 mg/L)
  - Fine particles
  - Dissolved acid gases (H_2S and CO_2)
  - Hardness from dissolved calcium and magnesium ions
  - Alkalinity from dissolved bicarbonate and carbonate ions
  - Trace elements, typically barium, lithium, potassium and strontium
  - Heavy metals
  - Naturally occurring radioactive materials (NORM)
    - Radium
    - Thorium
    - Uranium
- Other Constituents
  - Corrosion Inhibitors, Antiscalants, Biocides

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Produced Water Constituents (Source: Brine Chemistry Consortium, Rice University)

- NORM Chemistry
    - Produced water contains NORM at many locations depending upon geology
    - Most common constituents are Radium 226 and Radium 228
    - These are present in the form of $Ra2^{+}$ cations
    - Radium ions are mobile in water and present in concentrations from 0 to 1,000 pico curie/gram (pCi/gm)
    - Not enough to be regulated
    - If a produced water is scale forming NORM partitions into barite scale by co-precipitation: $Ba^{2+} + Ra^{2+} + SO_4^{2+} \rightarrow Ba(Ra)SO_4$
    - Estimated NORM accumulation rate in produced water scale in the US is 300,000 to 1,000,000 tons/year
    - For scales containing radiation level > 2,000 pCi/gm the rate drops to 15,000 to 50,000 tons/year
    - Barite has very low solubility and hard to remove without cutting
    - Storage and handling for disposal of radioactive materials with scale is a problem

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Produced Water Constituents

- Typical Composition of Produced Water

  pH = 6.5 to 8

  Oil & Grease = 9,500 mg/L

  TSS = 10,000

  TDS = 5%

  COD = 20,000 mg/L
- Composition can vary widely from one formation to another
- Methanol dosed only intermittently and at start-up
- Dosed methanol ends up in produced water and raises the COD levels exceeding 60,000 mg/L

Shale Gas: An Overview

- Natural gas from shale formations
- The shale acts as both the source and the reservoir for the natural gas
- Older shale gas wells were vertical
- Current wells are horizontal and need artificial stimulation, like hydraulic fracturing, to produce.

U.S. Shale Proved Reserves (Billion Cubic Feet)

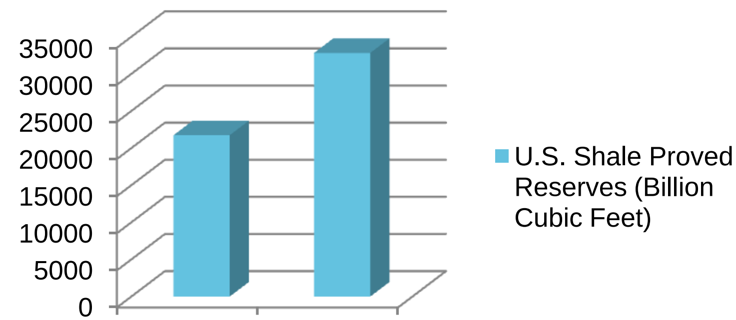
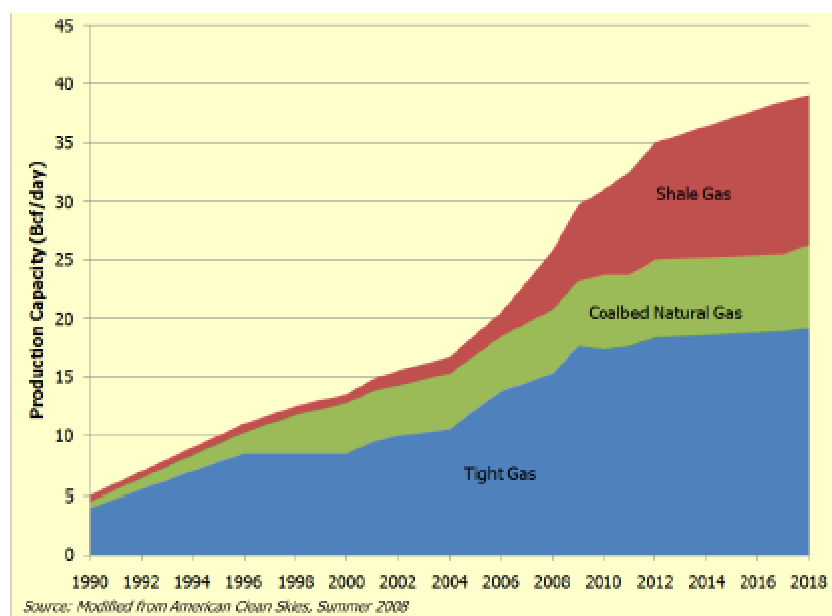
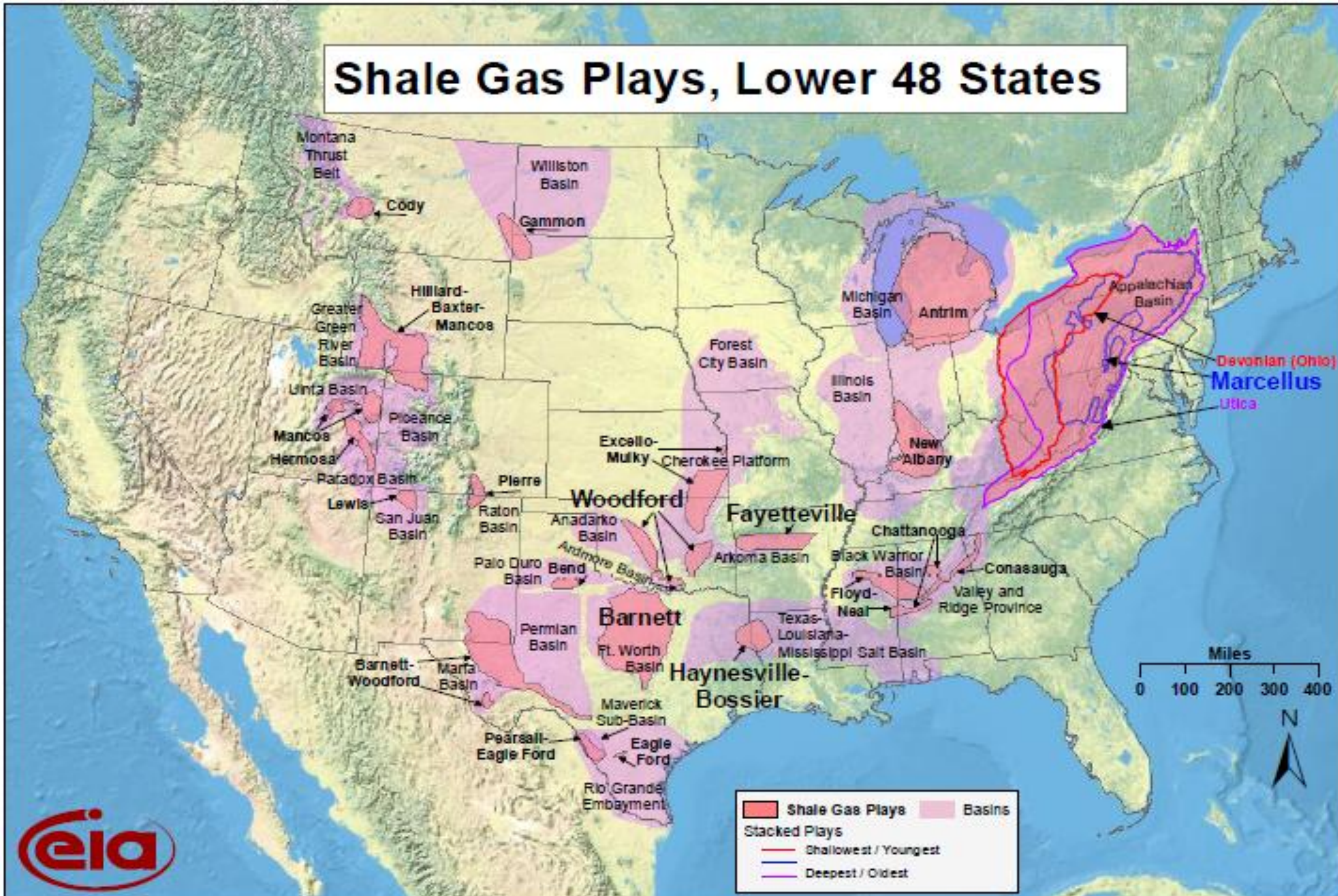


EXHIBIT 8: UNITED STATES UNCONVENTIONAL GAS OUTLOOK (BCF/DAY)



Shale Gas Situation in the United States



Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

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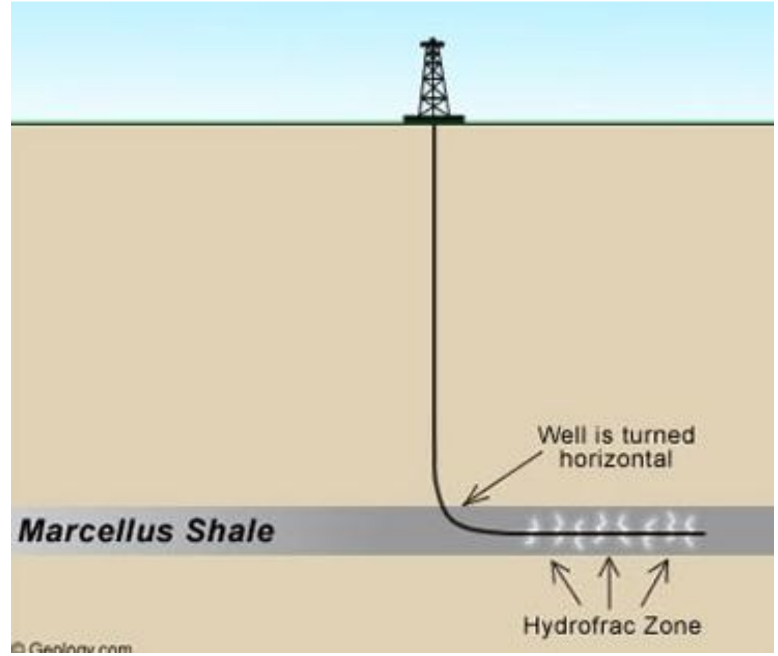
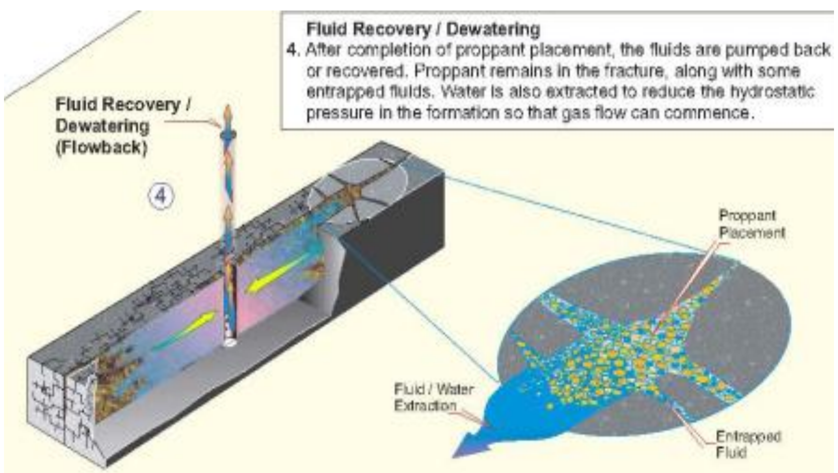
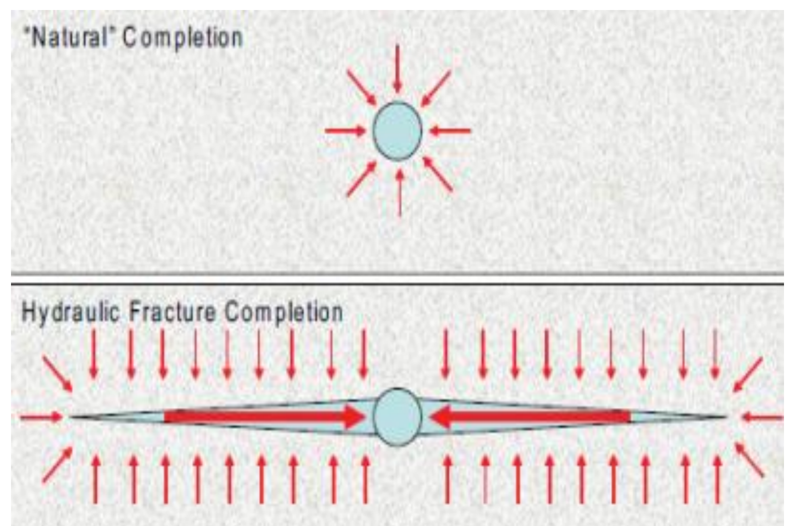
Production Method: – Hydrofracing

hydraulic fracturing or a *“hydrofrac,”* done by application of water under high pressure to fracture the rock and open it up by sand or other materials for gas to move to the well.

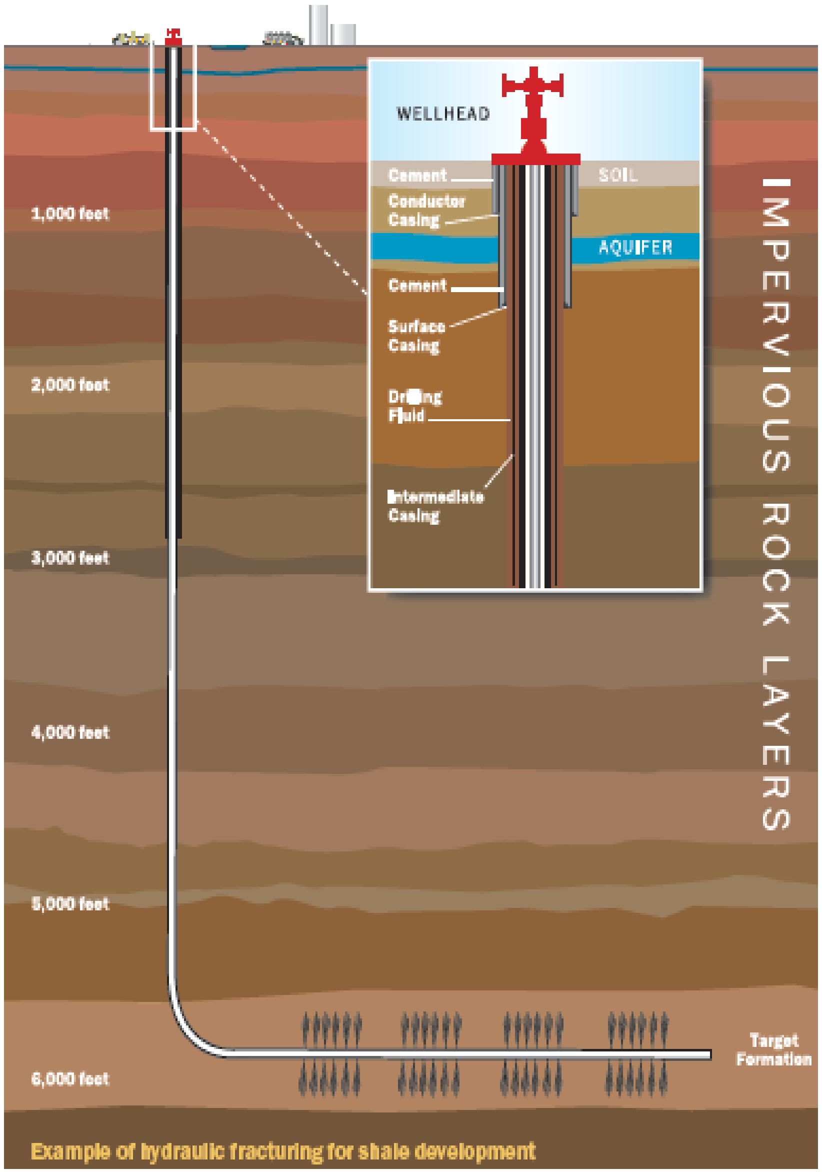






The BIG picture on Water needs

- In the U.S., an estimated 35,000 wells are hydraulically fractured annually
- Each frac needs 10,000 m^3 i.e. about 35,000 barrels of water .
- Some 10-15 fracs required for each well
- 100,000 m^3 of water will be required for each well
- 5 to 25% of Hydrofrac will be flowback to surface



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Marcellus Shale

- Estimated Basin Area = 246,000 sq. km (95,000 sq. miles)
- Depth = 1,200 – 2,600 meters
- Estimated Technically Recoverable Gas = 260 trillion cu. ft (tcf), or ~ 7.5 trillion cu. meter
- Estimated Water Requirement per well = 15,000 cu. meter

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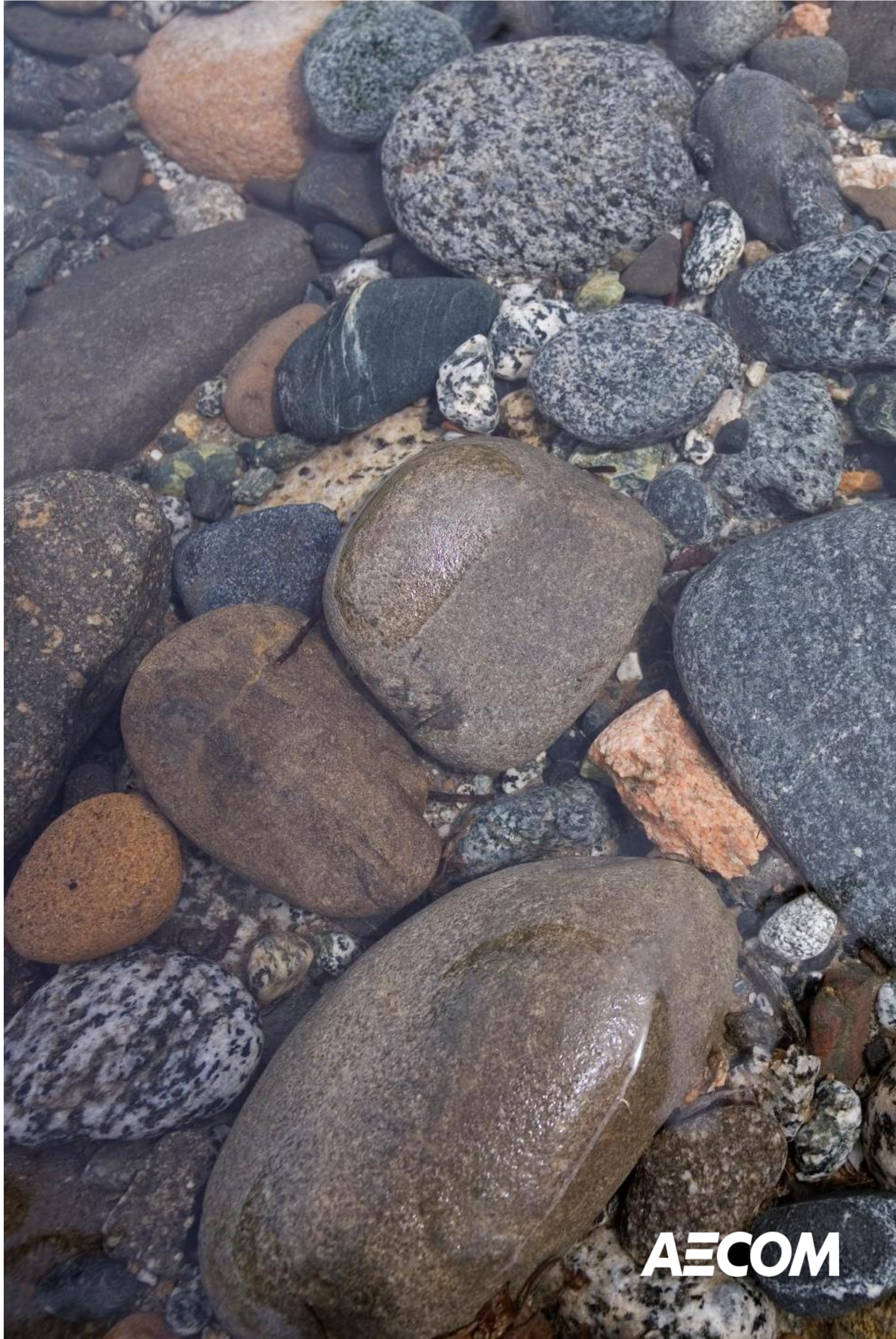
Water Sources

- Surface water,
- Groundwater,
- Municipal water suppliers,
- Treated wastewater from municipal and industrial treatment facilities,
- Recycled produced water and/or flow back water.

Concerns of Water-Resources

- Potential surface water degradation
- Potential groundwater contamination from hydraulic fracturing and disposal by injections
- Reduction in water supply due to withdrawal for fracturing purposes
- Reduced stream flow
- Aquifer depletion



Wastewater Issues

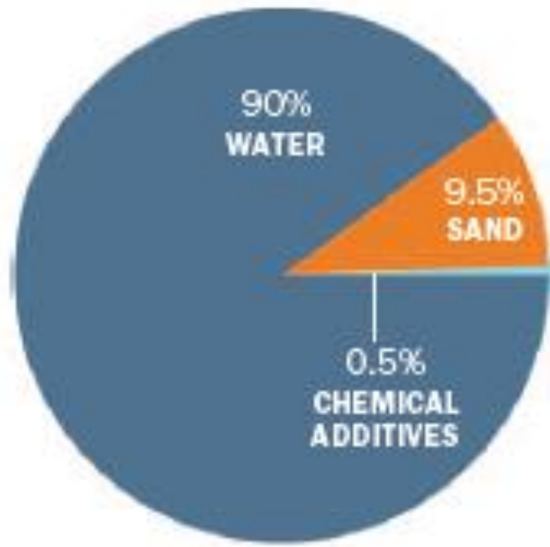
Hydrofrac Water

•Contains (See Table)

- Proprietary chemicals to increase the viscosity to a gel-like
- 0.5% additives (as listed on slide 4 and bottom of slide 10)
- *proppant*, usually sand, to keep fracture open

Flowback Water (see Table)

- Contains chemicals naturally occurring in the reservoir (TDS, TSS, TOC, NORM)
- Contains some of the constituents of frac water
- Needs proper management and disposal



Compound
Acids
Sodium Chloride
Polyacrylamide
Ethylene Glycol
Borate Salts
Sodium/Potassium Carbonate
Glutaraldehyde
Guar Gum
Citric Acid
Isopropanol

Frac Water Composition

(Source-Modern Shale Gas: A Primer, US DOE, '09)

Additive	Composition (% v/v)	Function
HCl (15% Solution)	0.123	Dissolve Minerals for Fracture
Glutaraldehyde	0.001	Biocide
Ammonium Persulfate	0.010	Emulsion Breaker
N, N Dimethyl Formamide	0.002	Corrosion Inhibitor
Borate Salts	0.007	Crosslinker to Maintain Viscosity
Polyacrilamide/Mineral Oil	0.088	Friction Reducer to Flow
Guar Gum (Hydroxymethyl Cellulose)	0.056	Gel to Suspend Proppant (Sand)
Citric Acid	0.004	Prevents Iron Precipitation
Potassium Chloride	0.060	Stabilizes Clay in shale formation
Ammonium Bislufite	0.002	Oxygen Scavenger to Prevent Corossion
Sodium/Potassium Carbonate	0.011	pH Adjusting Agent
Ethylene Glycol	0.043	Scale Inhibitor
Various Surfactants and Co-surfactant (Isopropanol)	0.085	Helps Improve Viscosity
Proppant (Sand)	0.500	Fracturing Agent
Water	99.5	Carrier Fluid

Typical Flowback Water Analysis at Marcellus Shale
(Source: Blauch, et al., SPE 125740, ‘09)

Flowback Vol (bbl)	12,000	13,000	14,000	15,000
pH	6.22	6.08	5.98	5.88
Alkalinity (HCO_3^- Only in mg/L of $CaCO_3$)	280	240	200	160
Cl^-, mg/L	54,000	59,000	62,900	67,800
SO_4^{2-}, mg/L	31	20	20	24
Na^+, mg/L	26,220	28,630	31,810	35,350
K^+, mg/L	1,119	1,201	1,350	1,480
Ca^{2+}, mg/L	7,160	7,680	8,880	9,720
Mg^{2+}, mg/L	341	463	488	805
Ba^{2+}, mg/L	28.9	43.3	99.6	175.7
Sr^{2+}, mg/L	1,110	1,305	1,513	1,387
Fe^{3+}, mg/L	0.4	0.9	1.1	3.3
Fe Total, mg/L	63	66	72	78
TSS, mg/L	144	175	498	502
Langelier Index	1.02	0.84	0.72	0.55
Microbial Count	Low	Low	Low	Low

Disposal of Flowback Water at Marcellus Shale

- Disposal in Class II Injection Wells
- Disposal to municipal wastewater treatment facilities, primarily in Pennsylvania
- On site centralized treatment facility to produce effluent of quality suitable for recycle and reuse
- Offsite Centralized Impoundment (generally not a disposal option, only a means for temporary storage)
- Radioactivity a concern at Marcellus Shale
- Geologic formation has high thorium, uranium and decay product Radium 226
- Ra 226 partitions into produced water and concentrates as it is reused several times
- NYSDEC estimates radionuclides in produced water at 15,000 pCi/L

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Applicable Regulations for Proper Disposal of Produced and Flowback Water

- For offshore production activities in US, requirements are covered under NPDES Oil & Gas Subcategory
- For fracing operations in US regulations vary from state to state.
- Regulations are very new in some states and developing in others
- The Commonwealth of Pennsylvania (PA DEP) recently imposed a limit of 500 mg/L of TDS from all industrial discharges that is applicable to Marcellus shale
- No EPA regulation yet on NORM in produced water scales, but Louisiana regulates radiation to a level of 50 μrems/hr and OSHA limit for worker exposure is 2,000 μrems/hr
- States that are currently enforcing or developing regulations include
  - New York (among others, the Draft Permit at Condition 31 (b) addresses the issue of dissolved radionuclides in liquid wastes for landfilling, but the same problem with solid wastes not considered)
  - Pennsylvania
  - West Virginia
  - Louisiana
  - Oklahoma
  - Wyoming

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Overview of Treatment Processes

- Overall treatment train
  - Physicochemical
    - Deoiling by API and IGF in series
    - Filtration
  - Biological – Main challenge is high salinity
    - Fixed Bed Aerated Biofilter
    - Granular Activated Carbon Fluidized Bed Reactor (GAC-FBR)
    - Moving Bed Bioreactor
    - Membrane Bioreactor
  - Physicochemical for final polishing for water recycle and reuse
    - Granular Activated Carbon (GAC)
      - To remove specific recalcitrant organic chemicals
      - Need prefiltration step if the biotreatment is not by MBR
      - Product can be recycled for fracing
    - Advanced Chemical Oxidation
      - By UV, or ozone + UV
      - Other aspects similar to treated product from GAC
    - Reverse Osmosis (RO), or Microfiltration (MF)
      - To remove TDS and organic residuals from biotreatment
      - Need prefiltration step if the biotreatment is not by MBR
      - Produces very high quality water usable for power generation

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Conclusions

- Dependence on natural gas as energy source increasing with respect to petroleum
- Newer technologies make it possible to tap natural gas from deep underground rock structures that were hitherto inaccessible
- This requires very large quantities of water for fracturing rock structures
- This water flows back as ‘Flowback’ water, which also includes “produced water” from underground
- It contains various heavy hydrocarbons and dissolved mineral salts from the produced water and chemical additives that are injected with “frac water’
- It is essential to treat this water for recycling it, or disposing it safely
- Treatment trains consist of combinations of physical, chemical and biological processes depending upon the chemical constituents of flowback water
- For Marcellus Shale, it is necessary to use an RO or MF membrane process at the end of the treatment train to ensure compliance with 500 mg/L TDS
- Disposal of the concentrate can only be done by evaporation/crystallization, which will produce 400 tpd of salt waste per 1 MGD of concentrate

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Thank You

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