A Biocide for Frac Water: How to manage microbiological performance with a “green” alternative biocide for re-use water

American Association of Drilling Engineers (*AADE*)

February 2012 – Houston Texas

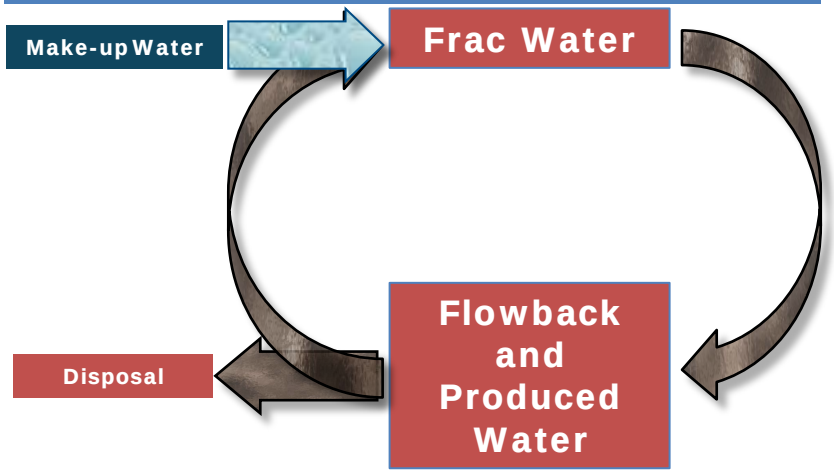
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Petroleum Industry : A New Perspective for Frac Water Biocide

- Driven by visibility of frac water and environmental public pressure
- Local and federal government engagement, studies, disclosure laws
- Industry desire to be more “green”
- Scarcity of water, and need to re-use water
- Disinfection By-Products (DBPs) are now a topic of discussion in petroleum industry
- Biocide must be both efficacious and meet environmental standards
- Petroleum industry continued desire for stewardship

Revolution in Water Re-Use

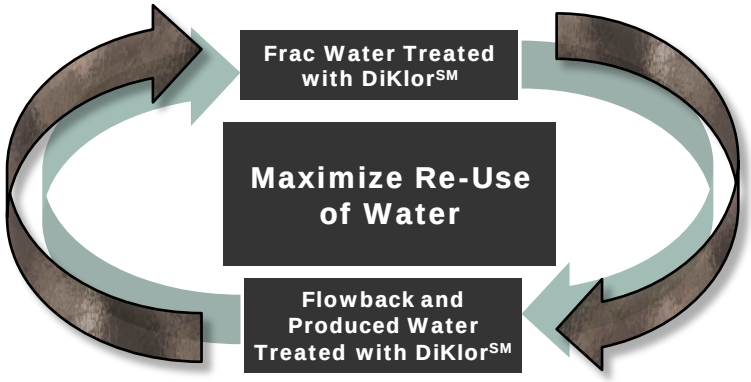
Traditional Water Life Cycle



Issues with Traditional Water Life Cycle

- To get fresh make-up water, companies incur significant sourcing and transportation costs
  - Transportation costs of several dollars per barrel
- During treatment, company must worry about possible contamination which leads to well damage or environmental issues
- After the flowback and produced water reaches the surface, companies must pay to store, clean and dispose of water
  - Average disposal fee of $2.00/barrel and transportation costs of several dollars per barrel

Sabre DiKlor^{SM} Closed-Loop Life Cycle



Solutions for Traditional Water Life Cycle

- **Sabre DiKlor^{SM} allows companies to safely re-use existing flowback and produced water, minimizing or replacing make-up water**
- **Treated water enhances well productivity and reduces potential environmental liabilities**
- **With safe and effective re-use of water, companies reduce the significant and increasing make-up and disposal costs for water**

Industry Challenges – Well Fracturing Water Re-Use

- Component concerns
  - Microbial
  - Inorganics
  - Organics
  - Brines and High TDS levels

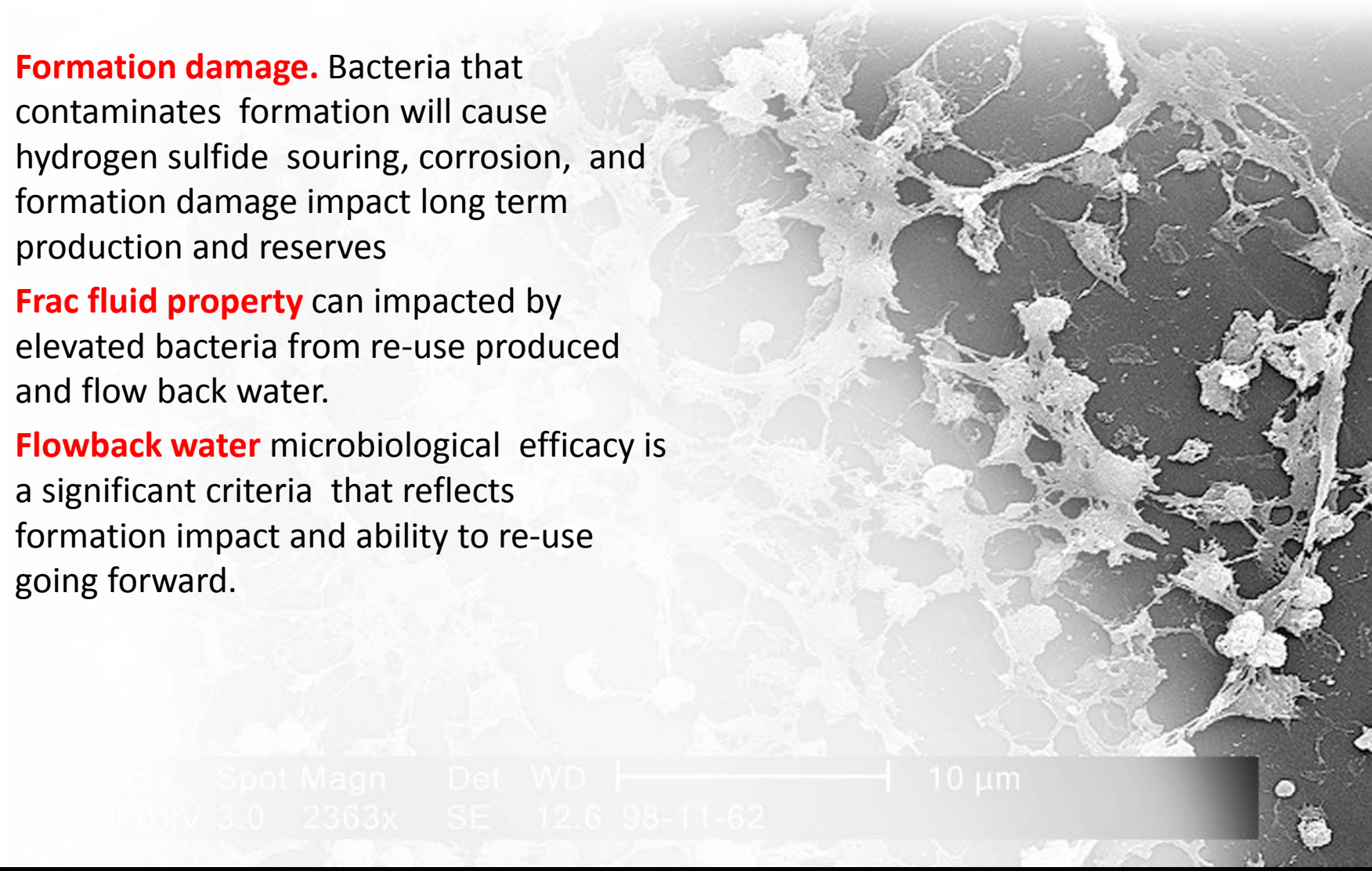
- Suitability for re-use
  - Environmental Compatibility
  - Formation Compatibility
  - Frac Fluid Formulation Compatibility
  - Scaling
  - Corrosion Control
  - Souring



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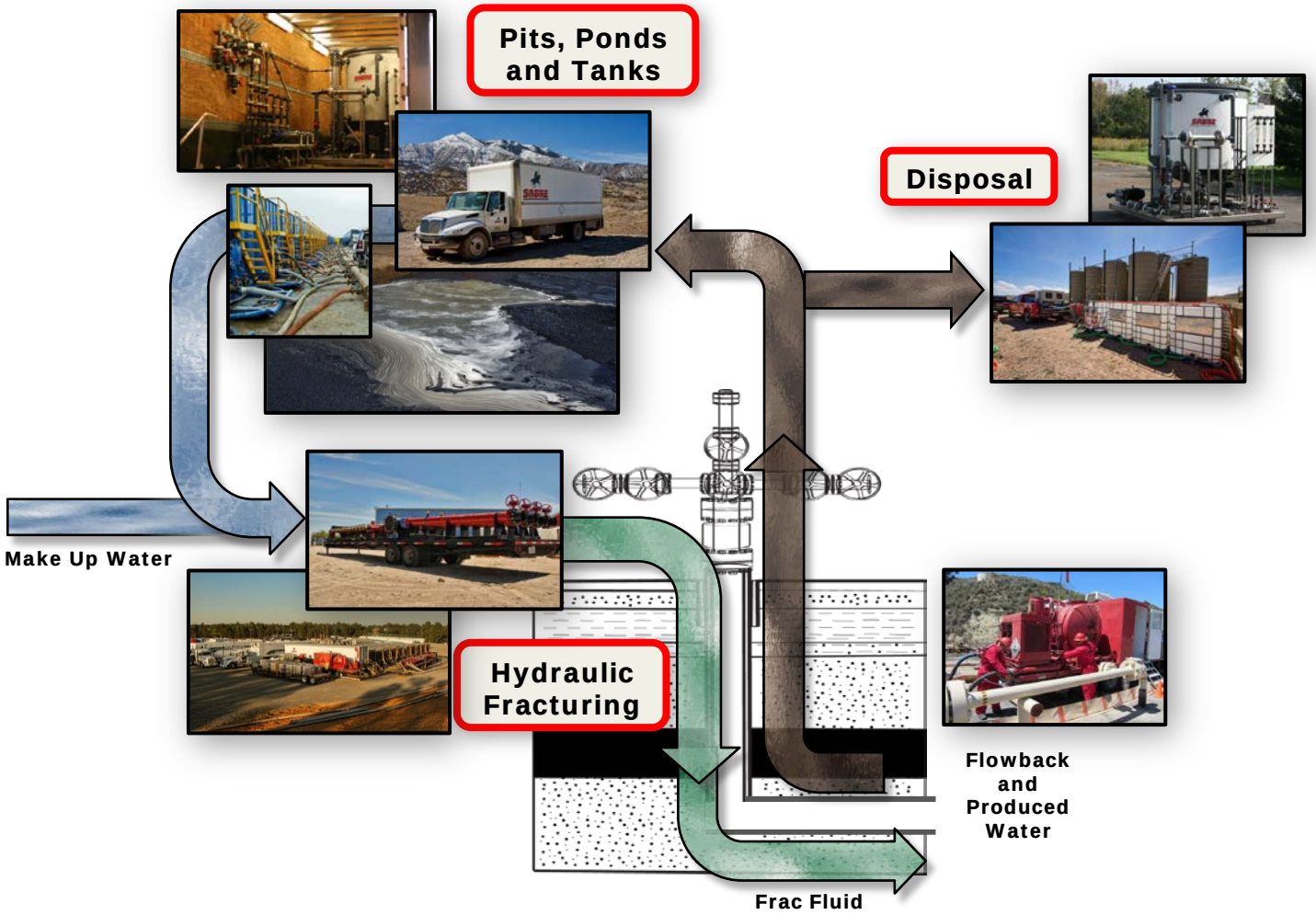
The Importance of Microbial Efficacy in Frac Water Re-use

- **Formation damage.** Bacteria that contaminates formation will cause hydrogen sulfide souring, corrosion, and formation damage impact long term production and reserves
- **Frac fluid property** can impacted by elevated bacteria from re-use produced and flow back water.
- **Flowback water** microbiological efficacy is a significant criteria that reflects formation impact and ability to re-use going forward.



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How can a biocide impact a water re-use program?



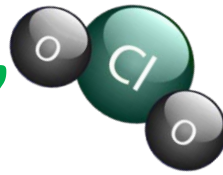
Typical Oil Field Biocide Options

- Non Oxidizers
  - Glutaraldehyde
  - THPS
  - Quaternary ammonium
- Oxidizers
  - Chlorine
  - Chlorine dioxide (DiKlor ^{SM} technology)
  - Peracetic acid, Sodium bromide, bleach, ozone
- Non oxidizers typically have a slower microbial kill and more persistent and more common in oil field, but are being scrutinized
- Oxidizers are considered to be fast kill and significantly more reactive and less persistent. Oxidizers are gaining position due to improved efficacy and environmental benefits

Future Considerations in Selection of Biocides

- pH, temperature, water chemistry and level of contaminations
- Oxidizers are expected to have a greater presence in oil field in future, particularly in frac water due to environmental benefits
- Less persistent chemistry will be preferred and demanded by public
- Efficacy will be examined more to optimize applied dosage and maximize reservoir microbial protection
- Potable approved oxidizers and safe drinking water approvals will drive biocide selections

The “Chlorine Dioxide Approach”



- An oxidizing biocide that potable water approved and is with safe drinking water standards
- Sabre DiKlor^{SM} is pure ClO_2 as produced using Sabre’s patented process.
- Pure ClO_2 is a water-soluble gas with a slight yellow-green color with a broad pH efficacy range
- Treats water at up to 300 barrels/minute
- Generated on-site using mobile units that have proven durability in oilfield conditions with a small site footprint
- Capable of utilizing dirty water and water of varying pH
- Not a persistent biocide

History of Chlorine Dioxide

- Used in Drinking water since the 1940s as an alternative to Chlorine.
  - No THMs, bromate by-products.
  - Currently consumed by 12% of USA drinking water population
- Pulp bleaching industry standard. Industry converted to chlorine dioxide to reduce environmental impact, and improve brightness.
- Used in food processing industry for over 30 years. FDA considers many applications as Generally Recognized As Safe(GRAS). Many uses in industrial markets
- Sabre has been committed to the use of chlorine dioxide in the petroleum industry since 1988.
- Diklor ^{SM} is a patented Sabre process technology. It is the result of many years of experience in the oilfield.

Chlorine Dioxide Chemistry

- A dissolved gas in water
- Does not hydrolyze in water
- No production of bromide, bromate, aldehydes, ketones, tri-halomethanes (THM). These are key chemistry drivers that allow for use in drinking water disinfection.
- Does not require high residual concentrations
- Low corrosivity as compared to other oxidants

Chlorine Dioxide Effectiveness

- Does not require long residence time in tanks or pits to achieve desired efficacy.
- Performs in a wide pH range (<10)
- Penetrates cell wall of microorganisms
- Prevents organisms from building a resistance
- Eliminates bio-film on process surfaces
- Removes iron and manganese
- Eliminates H_2S

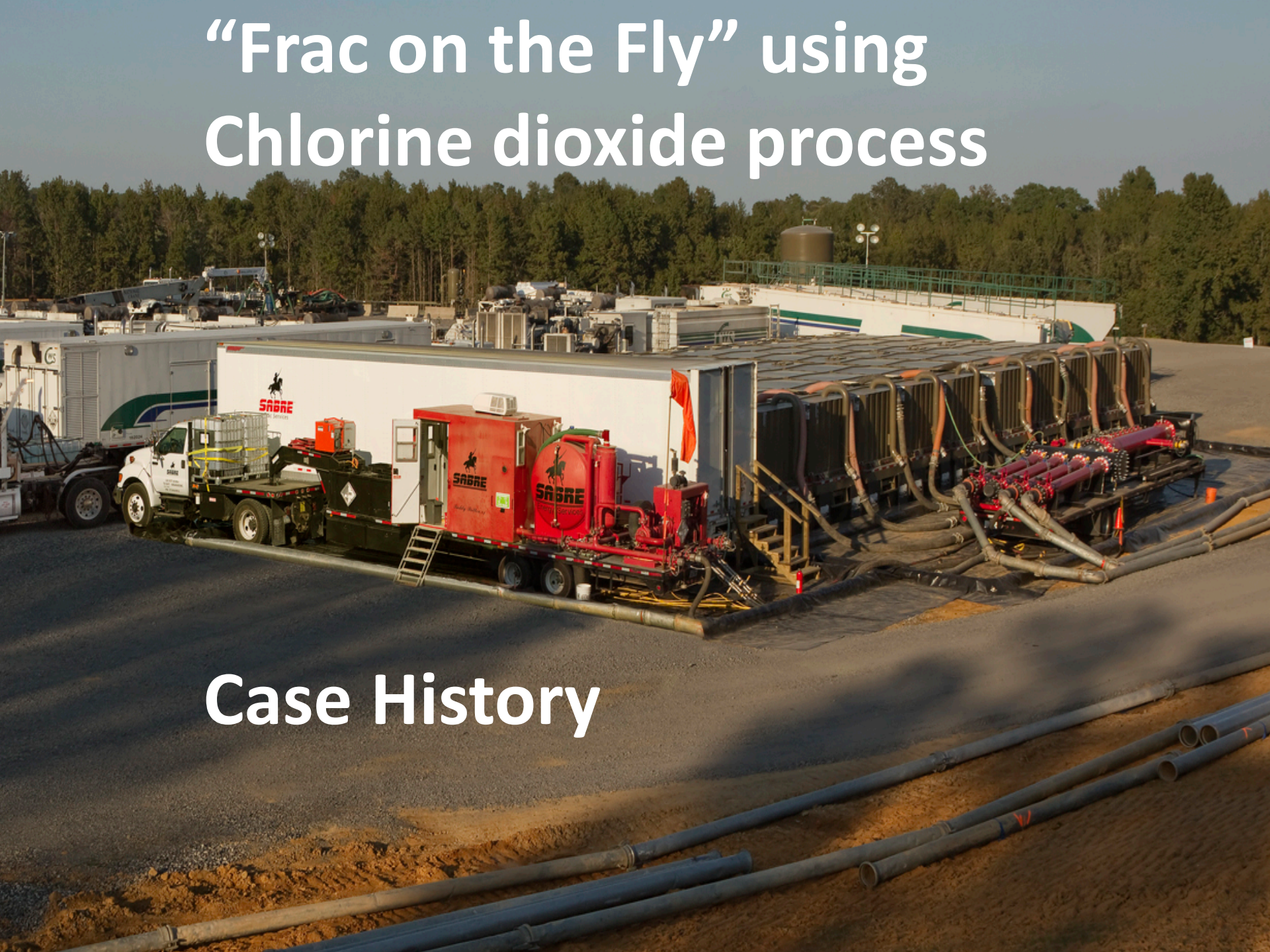
Safety

- Chlorine dioxide is a dissolved gas that used below solubility at all times.
- Excellent safety record in the handling of the chemicals and equipment
- Process and reaction chemistry under vacuum conditions is preferred
- Potable water approved for consumptions.
- Process is PHA compliant.
- Air quality testing is excellent



Safety Matters to Sabre

“Frac on the Fly” using Chlorine dioxide process



Case History

Frac on the Fly

- A novel approach that re-uses multiple water sources to frac wells
- Water sources may be produced, surface, flow back, pits
- Treatment is “on the fly” as the frac proceeds
- Water treatment capacity is up to 300 BPM at a frac on the fly injection rate ~100 BPM, minimal foot print
- Automated and manual process control
- Disinfection is immediate with excellent microbial surface water disinfection going down hole.
- Excellent efficacy with 7 day, 14 day, 28 day testing.

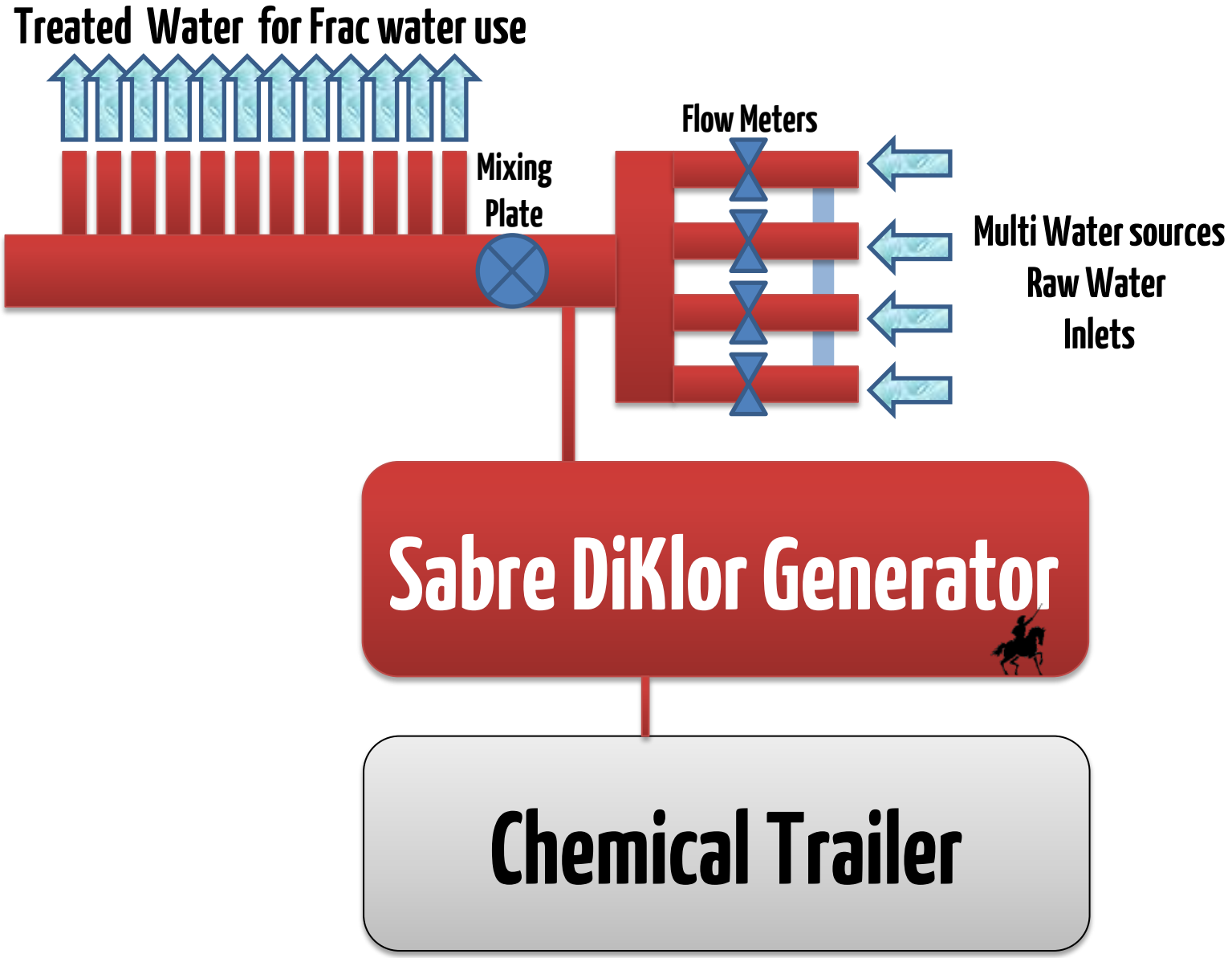
Chlorine Dioxide
Benefits For Frac Water re-use

- Efficacious Biocide with favorable regulatory status under the **Safe Drinking Water Act**
- Enables the separation and concentration of **metals of concern through oxidation**
- Enables **separation of hydrocarbons and organics of concern**, including so called soluble hydrocarbons by destruction of micro-emulsions and reverse emulsions through selective oxidation and wetability changes.
- Regulatory Status **simplifies permitting procedure**
- **Excellent flowback** microbiological efficacy to maximize production

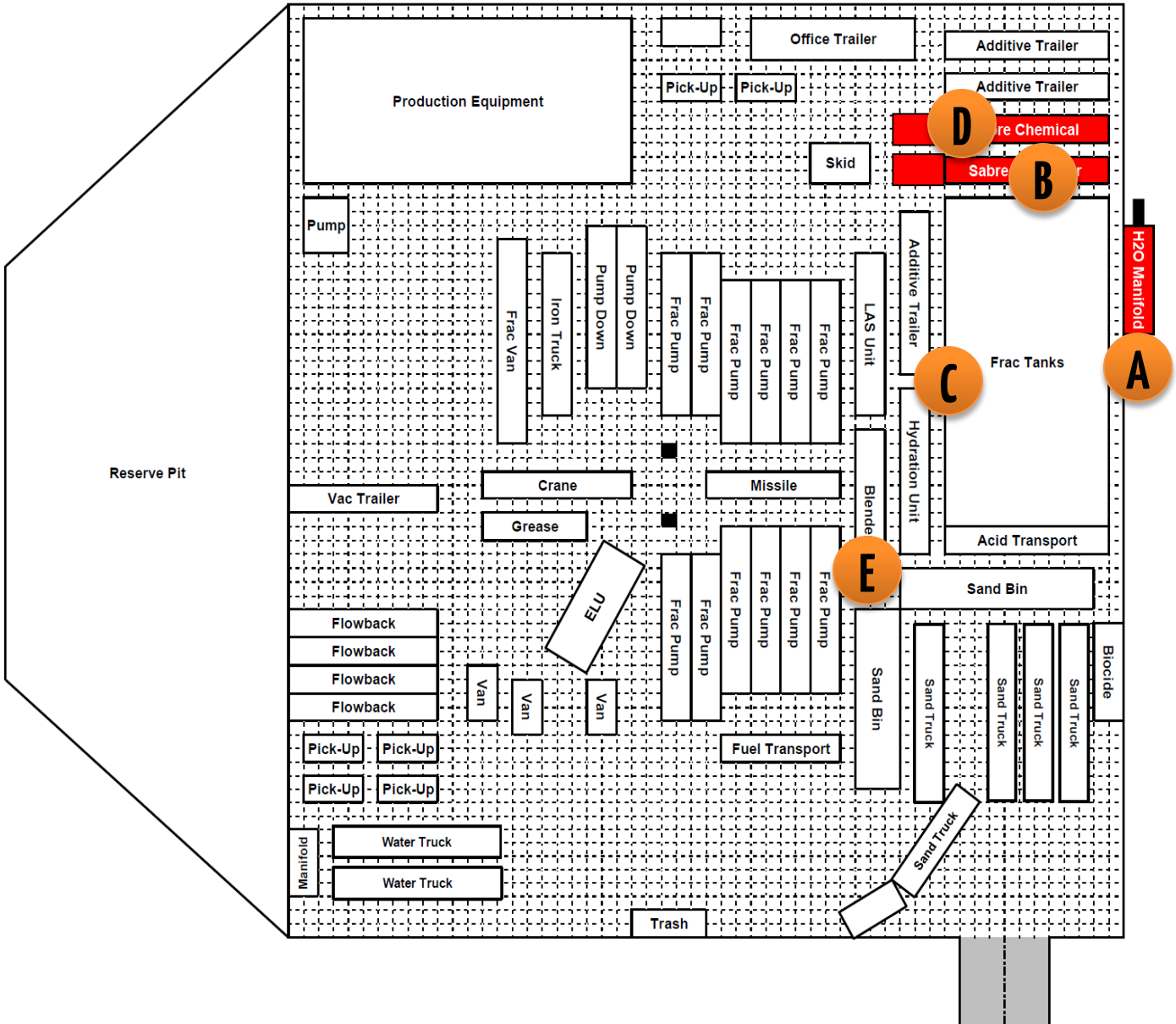


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Frac on-the-fly Process Flow



Process Control



A. Raw Water
B. Generator
C. Post Frac Tanks
D. Chemical Staging
E. Post Blender

Surface Water Treatment Results Comparison

Illustration of results based on laboratory testing performed by Oil and Gas Operator

Surface Water Treatment Results

Untreated		**6+ log bacterial contamination**
Treated with Conventional Biocides or Ozone		**3- to 4-log reduction but greater than 100,000 cfu / ml of bacterial contamination remains**
Treated with Sabre DiKlor℠		**NO GROWTH—No bacterial contamination remains**

Flow back Results – 30 day Comparison

Flowback Water Treatment Results – 30 Days

30-day results after frac water has been treated with alternatives; indicator of future bacterial well damage leading to impaired production, and souring of formation leading to higher production costs

Treated with Conventional Biocides or Ozone



Greater than 6-log bacterial contamination— No evidence of any reduction from treatment

Treated with Sabre DiKlor℠



AT LEAST 100,000-FOLD REDUCTION in bacterial contamination in flowback water

Thank you

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