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Contributing Anthropogenic Factors to H_2S Generation in Northern Athabasca Aquifers

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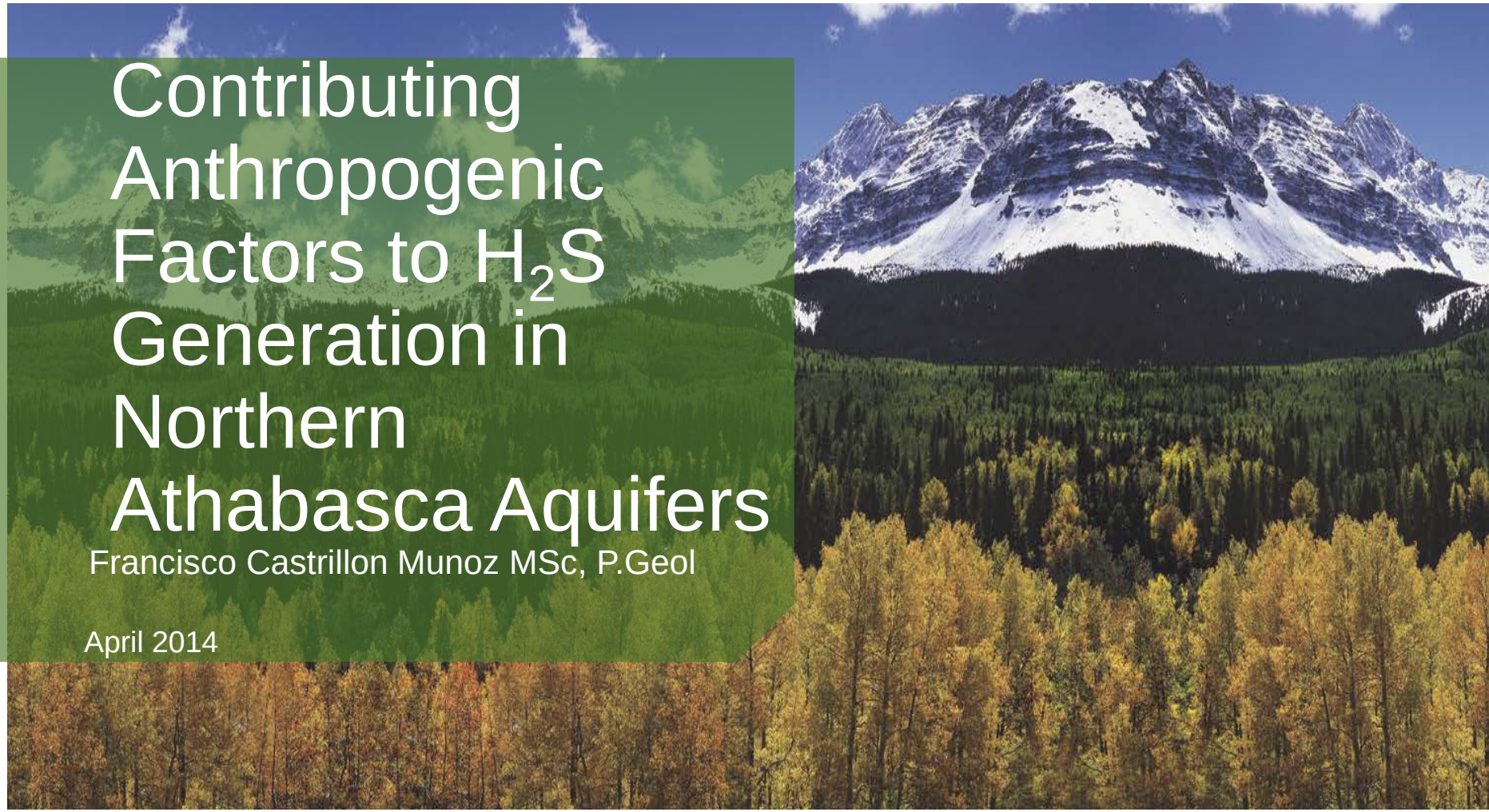


EcoNomics

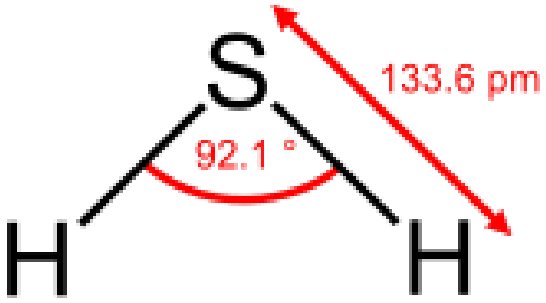
Motivation

- The presence of H_2S poses significant risks to contractors and to the integrity of drilling infrastructure on site and causes drilling delays (emergency shut downs);
- It is a frequent assumption that all H_2S found during drilling is generated within the reservoir. Although this may be true in most cases, anthropogenic actions can also generate H_2S within the wellbore annular space

This presentation

- Introduction – properties & toxicity
- summarizes the natural origin and systematics of H_2S;
- defines several anthropogenic factors associated with the presence of H_2S; and
- suggests measures to potentially reduce the generation of H_2S concentrations during well development.

Physical & Chemical Properties - H_2S (gas)



pm: Picometers = 10^{-12} meters

- Molecular Formula: H_2S
- Molar Mass: 34.08 g/mol (H_2O= 18.0 g/mol)
- Appearance: Colourless gas
- Odour: faint rotten egg
- Density: 1.363 g/dm^3
- Solubility in water: 4 g/dm^3
- Heavier than air
- Autoignition: 232^{o}C

Alberta Energy Resources (AER) defines H_2S as a naturally occurring, highly toxic, corrosive, gas with the odour of rotten eggs, and sour gas as a raw natural gas with a relatively high concentration of sulfur compounds including H_2S.

Toxicity - H_2S (gas)

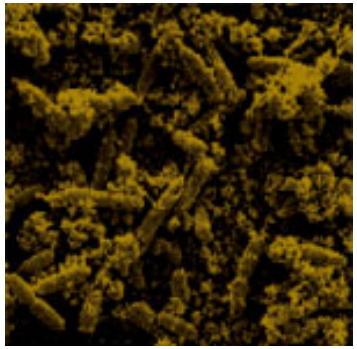

- OSHA has established a permissible exposure limit (PEL) (8 hour time-weighted average (TWA)) of 10 ppm;
- 50–100 ppm leads to eye damage;
- 150 ppm can paralyze the olfactory nerve
- 530–1000 ppm causes strong stimulation of the central nervous system and rapid breathing, leading to loss of breathing; and
- 800 ppm is the lethal concentration for 50% of humans for 5 minutes exposure (LC50);

Natural origin and systematics of H_2S

H_2S Presence in Groundwater

$CaSO_4 .H_2O$
$CaSO_4$

CH_2O



Sulfate-reduction facultative bacteria

- Frequently detected during drilling, and well workover activities;
- It can occur naturally dissolved in groundwater present in oil sands Fms. & other **formations** in the Northern Athabasca Region, Alberta;
- About 30% of Canada's natural gas production is sour and most of it is found in Alberta and Northeastern British Columbia;

http://www.capp.ca/environmentCommunity/airClimateChange/Pages/SourGas.aspx

H_2S Presence in Groundwater

- H_2S Can be generated through three main mechanisms:

- Chemical sulfur reduction (CSR)
- Biological sulfate reduction (BSR)
- Thermal sulfate reduction (TSR)

H_2S Generation - Pyrite dissolution (CSR)

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

$$FeS_2 + 14FeOOH + 26H^+ \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 20H_2O$$

Sulfur associated minerals (pyrite, pyrrhotite) dissolution can contribute to the occurrence of sulfate in groundwater;

$$FeS_2 + 4HCl \text{ '} \quad Fe^{2+} + 4Cl^- + 2H_2S(g)$$

Well acidification in presence of pyrite

- **Pyrite dissolution** (FeS_2) is minor in carbonatic formations but it is commonly found in other oil sands environments

H_2S **Generation** - Redox Mediated Process (BSR) Gypsum dissolution

$$CaSO_4(2H_2O) + H_2O” \quad Ca^{2+} + SO_4^{2-} + 3H_2O$$

- dissolved sulfate frequently increases in native carbonatic formation water.

Gypsum ($CaSO_4(2H_2O)$) and anhydrite ($CaSO_4$), are the principal constituents of marine evaporites and major contributors to the occurrence of sulfate in groundwater

H_2S Generation – Sulfate Reduction - Redox Mediated Process (BSR)

$$CaSO_4(2H_2O) + H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 3H_2O$$

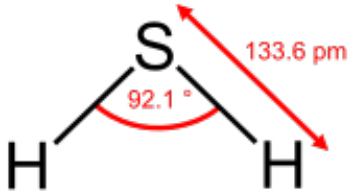
$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

- this reaction is mediated by microbial metabolism
- proceeds primarily from organic matter (CH_2O)
- Carbonatic Formations may contain natural organic matter or may originate from using process water, boiler feed water, or wastewater injection.

H_2S Generation - Thermochemical Reduction of Sulfate (TSR)

+ SO_4^{2-} +

=

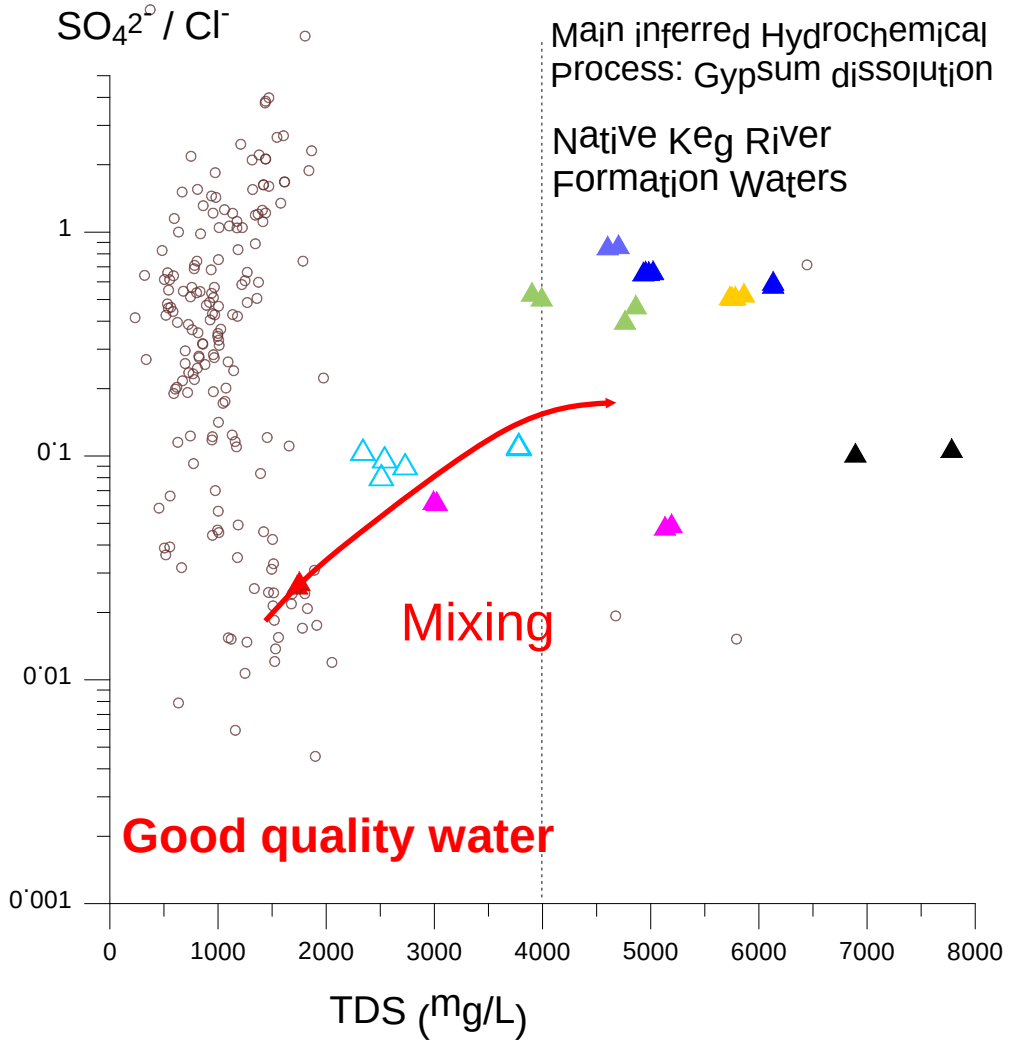


$R\text{-}CH_3 + 2R{=}CH_2 + CH_4 + 3SO_4^{2-} + 5H^+ \rightarrow 3R\text{-}COOH + HCO_3^-/CO_2 + 3H_2O + 3H_2S/HS^-$

- Thermal decomposition of organic sulfur starts at 200ºC;
- Thermochemical reduction of sulfate (TSR) starts at temperatures of 100ºC-140ºC; and
- this reaction is controlled by the temperature, type of organic material and concentration of sulfate (Mayrhofer et al 2014).

Anthropogenic factors associated with the presence of H_2S

Disposal Injection



SO_4/Cl (meq/L) ratios in limestone water, if high (>1), may suggest sulfur oxidation processes occurring.

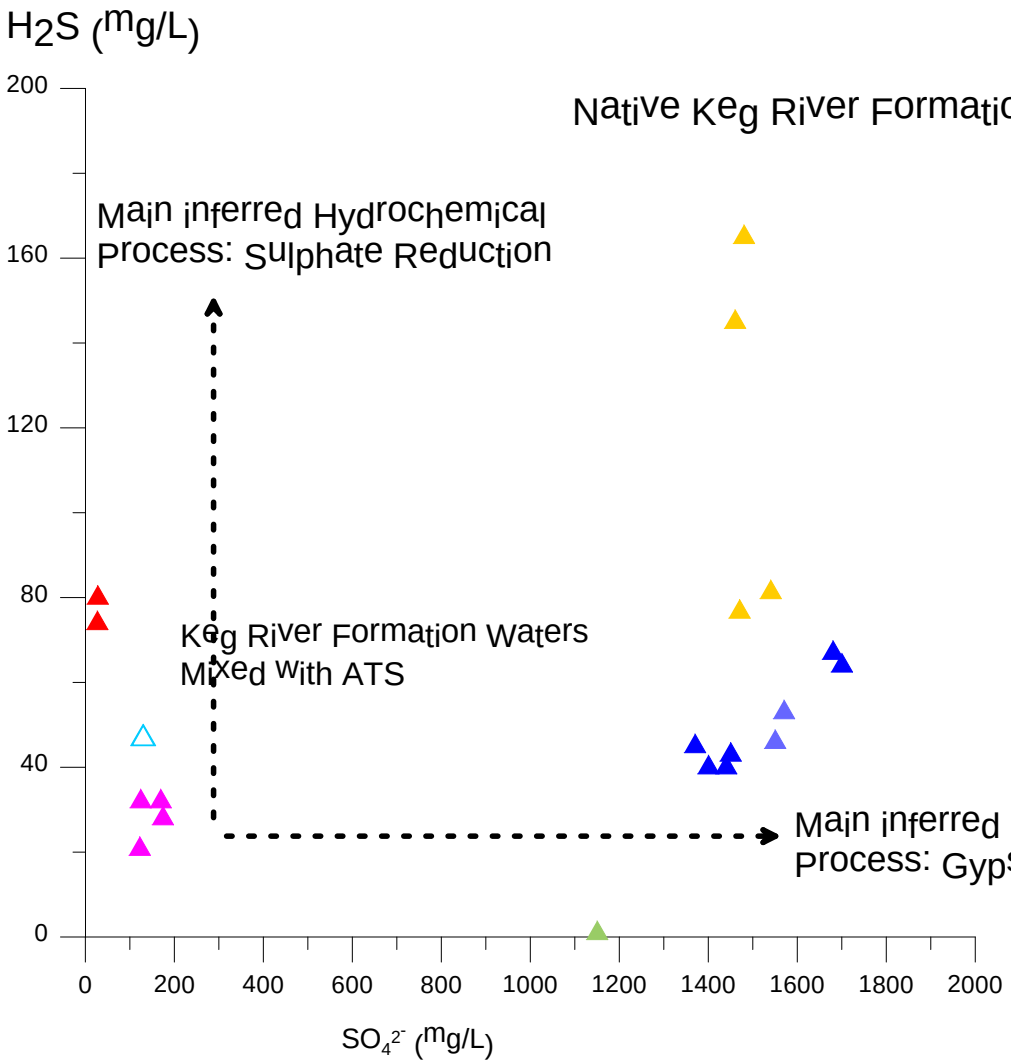
Sulfate oxidation may be naturally buffered by the presence of limestone dissolution as a result of well acidification.

Gypsum dissolution:
$CaSO_4(2H_2O) + H_2O$" $Ca^{2+} + SO_4^{2-} + 3H_2O$

Sulfate reduction:
$2CH_2O + SO_4^{2-}$ ' $2HCO_3^- + H_2S$

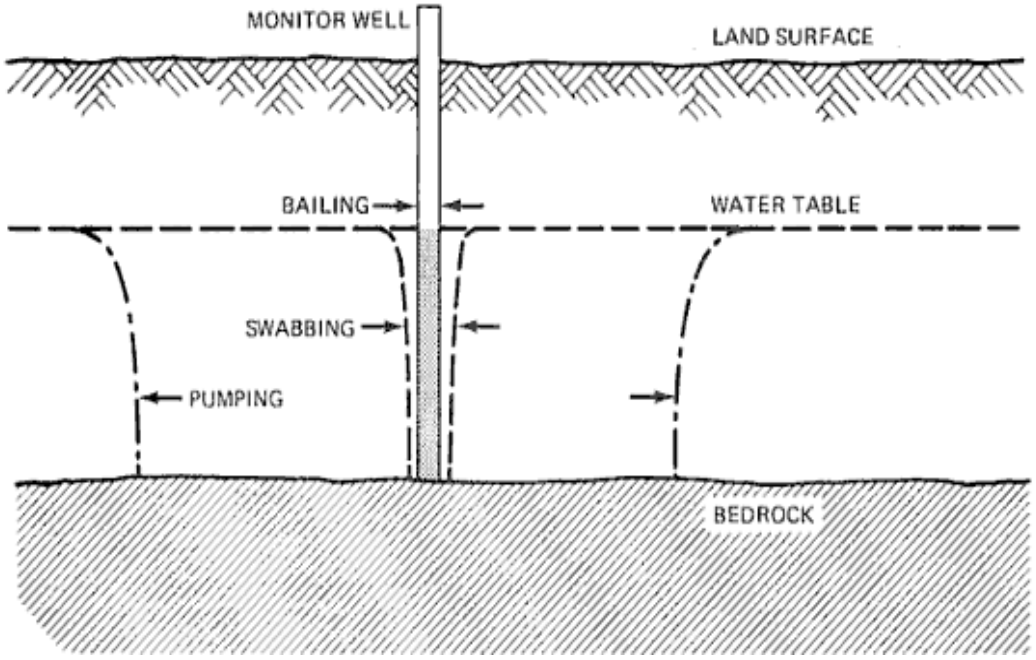
Taken from: http://www.esaaevents.com/proceedings/watertech/2012/pdf/P26.pdf.

Disposal Injection



Sulfate oxidation may be naturally buffered by the presence of limestone dissolution as a result of well acidification.

Wellbore Stimulation



eventually non fresh and clean water is available for wellbore stimulation (CH_2O)

presence of dissolved sulfate may be expected in carbonatic formations

anthropogenic H_2S might be produced

- Warm water

H_2S usually flourish in oxygen-deficient environments and in warm/hot waters (between 30°C and 80°C)

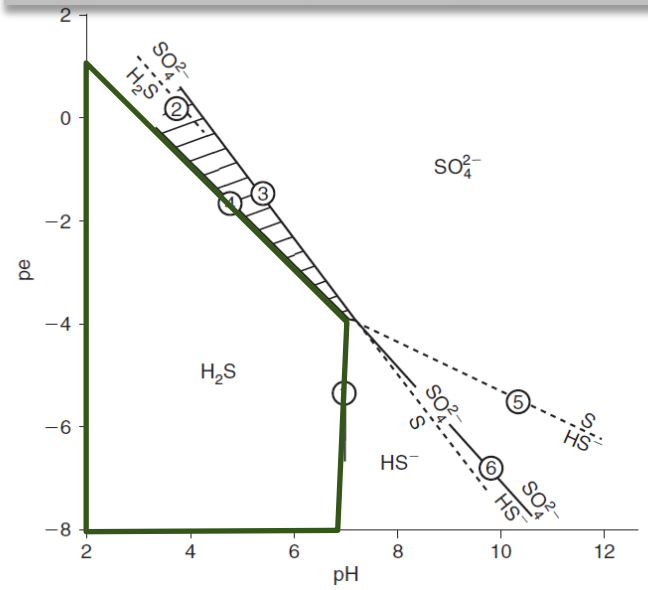
- Acid enhancing stimulation

$FeS_2 + 2HCl$ ' $Fe^{2+} + 2Cl^- + H_2S(g)$

$CaSO_4 + 2HCl$ ' $CaCl_2 + H_2SO_4$

H_2SO_4 " $2H^+ + SO_4^{2-}$

$CaCO_3(s) + 2HCl$ ' $Ca^{2+} + H_2O + 2Cl^- + CO_2(g)$

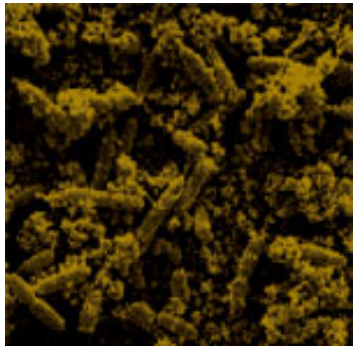


Conclusions

Assess the risks to H_2S generation

$CaSO_4 .H_2O$
$CaSO_4$

CH_2O



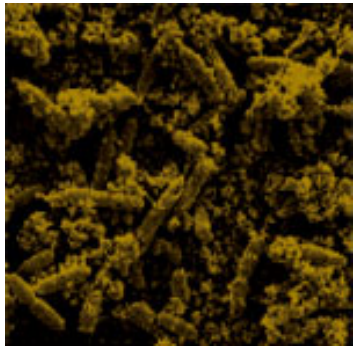
Sulfate-reduction facultative bacteria

1. **Define the mineralogy of your formation(s) prior to developing a workover program;**
2. **Characterize the source water chemistry to be used during your workover program;**
3. **Define your native formation water chemistry;**
4. **Forecast the H_2S production during workover by applying kinetic tools to include H_2S distribution over the fluid phases within the wellbore**

If you find potential for H_2S generation then

$CaSO_4 .H_2O$
$CaSO_4$

CH_2O



Sulfate-reduction facultative bacteria

1. **Consider opportunities for decreasing acidification volumes;**
2. **Consider decreasing the injection of warm / hot water during workover particularly after acidification injection;**
3. **Assess the option of using an H_2S scavenger**
4. **Work in coordination with your drilling operators**

These measures not only will help you to improve the H&SE scenario but also reduce operational cost due to reduced well shut downs and vac trucks utilization


Thank you.