DISPOSAL OF PRODUCED WATER INTO DEPLETED OIL RESERVOIRS: ECONOMIC USE AND RISK OF USDW POLLUTION

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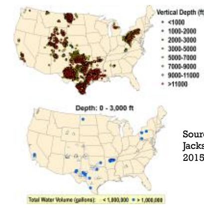
LOCATION AND DEPTHS OF HYDRAULIC FRACTURING ACROSS THE UNITE STATES

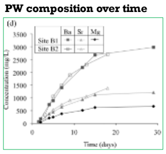
- The average fracturing depth across the US is 2500 m
- Many wells (6900; 16%) were fractured less than 1600 m
- 2600 wells (6%) were fractures above 900 m



Source: R. B. Jackson et al., 2015

CHEMICAL COMPOSITION OF PRODUCED WATER (PW)

PW composition over time



Source: E. Barbot et al., 2013

- TDS include heavy metals and NORMs
- Organic matter includes organic fracturing additives (e.g., guar gum)
- Ba is the most common and abundant heavy metal found in PW from hydraulically fractured shale gas reservoirs

Table 1. Summary of Marcellus Shale Produced Water Quality in Pennsylvania

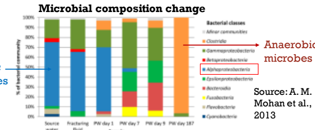
Source: E. Barbot et al., 2013

	minimum	maximum	average	number of samples
TDS (mg/L)	680	345,000	106,390	129
TSS (mg/L)	4	7,600	352	156
oil and grease (mg/L)	4.6	802	74	62
COD (mg/L)	195	36,600	15,358	89
TOC (mg/L)	1.2	1530	160	55
pH	5.1	8.42	6.56	156
alkalinity (mg/L as $CaCO_3$)	7.5	577	165	144
SO_4 (mg/L)	0	763	71	113
Cl (mg/L)	64.2	196,000	57,447	154
Br (mg/L)	0.2	1,990	511	95
Na (mg/L)	69.2	117,000	24,123	157
Ca (mg/L)	37.8	41,000	7,220	159
Mg (mg/L)	17.3	2,550	632	157
Ba (mg/L)	0.24	13,800	2,224	159
Sr (mg/L)	0.59	8,460	1,695	151
Fe dissolved (mg/L)	0.1	222	40.8	134
Fe total (mg/L)	2.6	321	76	141
gross alpha[a] (pCi/L)	37.7	9,551	1,509	32
gross beta[a] (pCi/L)	75.2	597,600	43,415	32
Ra^{228} (pCi/L)	0	1,360	120	46
Ra^{226} (pCi/L)	2.75	9,280	623	46
U^{235} (pCi/L)	0	20	1	14
U^{238} (pCi/L)	0	497	42	14

MICROBIOLOGICAL COMPOSITION OF PRODUCED WATER FROM SHALE GAS RESERVOIRS

- Biocide treatments are not effective in suppressing microbial activity
- The relative abundance of aerobic microbial species decreases in produced water with an increase in anaerobic microbial species

Microbial composition change

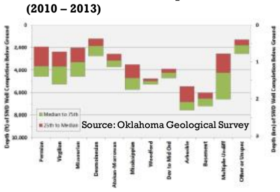


Source: A. M. Mohan et al., 2013

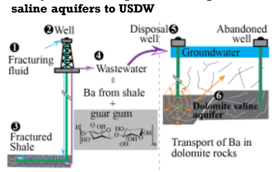
Stored produced water

RISK OF USDW CONTAMINATION BY HEAVY METALS PRESENT IN PRODUCED WATER?

Depths below surface, for completion intervals of saltwater disposal wells (2010 – 2013)



Possible pathways for heavy metals transport from deep saline aquifers to USDW

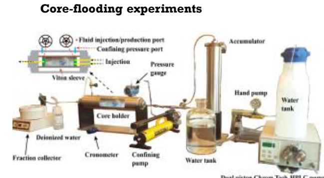


USDW: Underground Source of Drinking Water

EXPERIMENTS TO DETERMINE THE MOBILITY OF HEAVY METALS (BARIUM) IN DISPOSAL SITES

Batch sorption experiments

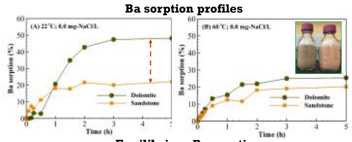
Core-flooding experiments



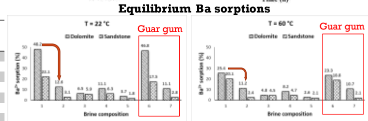
SORPTION OF BARIUM ON DOLOMITE AND SANDSTONE

- Ba sorption decreases with increasing salinity and temperature
- Ba sorption is higher on dolomite than on sandstone

Ba sorption profiles



Equilibrium Ba sorptions

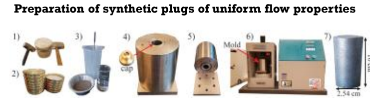


Tested PW compositions

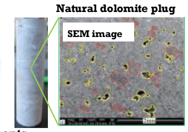
	NaCl (mg/L)	Ca (mg/L)	Mg (mg/L)	Guar gum (mg/L)
1	0.0	0.0	0.0	0.0
2	90,000	0.0	0.0	0.0
3	0.0	1,000	0.0	0.0
4	0.0	0.0	1,000	0.0
5	90,000	1,000	1,000	0.0
6	0.0	0.0	0.0	50
7	90,000	0.0	0.0	50

PREPARATION OF NATURAL AND SYNTHETIC CORE PLUGS

Preparation of synthetic plugs of uniform flow properties



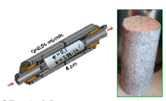
Natural dolomite plug



Flow properties of core plugs used for core-flooding experiments

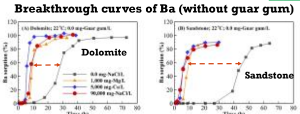
Core plug type	Grain size (μm)	Diameter (cm)	Length (cm)	Porosity (%)	Permeability (mD)
Natural dolomite	125-500	2.54	4	5-9	0.06-0.4
Synthetic dolomite	500-600	2.54	7.4	26.1	12.2
Synthetic sandstone	500-600	2.54	8.8	32.5	108.7

MOBILITY OF BARIUM THROUGH DOLOMITE AND SANDSTONE ROCKS

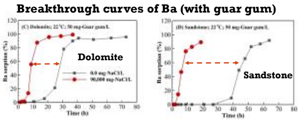


- Ba mobility increases with increasing NaCl, Ca, and Mg concentrations
- Ba mobility is higher in dolomite aquifers than in sandstone aquifers
- Compared to the effect of salinity, guar gum has a negligible effect on the mobility of Ba

Breakthrough curves of Ba (without guar gum)



Breakthrough curves of Ba (with guar gum)



STIMULATION OF METHANOGENIC CRUDE OIL BIODEGRADATION?

Target microorganisms

- Sulfate reducing bacteria (SRB)
- Nitrate reducing bacteria
- Fermentative microbes
  - Hydrogen forming microbes

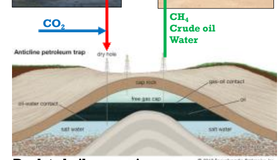
    $4C_{16}H_{34} + 64H_2O \rightarrow 32CH_3COO^- + 32H^+ + 68H_2$
- Consortia of methanogenic microbes
  - Acetoclastic methanogens

    $32CH_3COO^- + 32H^+ \rightarrow 32CH_4 + 32CO_2$
  - Hydrogenotrophic methanogens

    $196H_2 + 64CO_2 \rightarrow 49CH_4 + 15CO_2 + 98H_2O$

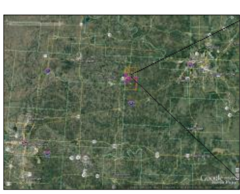
Stored produced water

Three-phase separator



Depleted oil reservoir

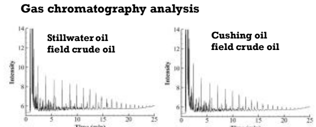
STUDY CASE: STILLWATER AND CUSHING OIL FIELDS OF OKLAHOMA



Cushing oil field in Oklahoma

PRODUCED WATER AND CRUDE OIL COMPOSITION

Gas chromatography analysis

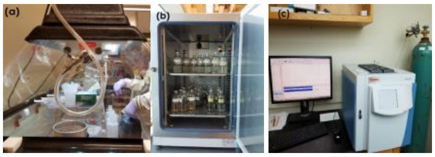


- Both crude oils resemble waxy crude oil containing high concentrations of heavy n-alkanes (C_{18+})

Chemical composition of PWs

Element	Stillwater (mg/L)	Cushing (mg/L)
Cl	73,064	110,699
NO_3^{3-} - N	0.3	0.13
Na	35,326	53,011
Ca	6,913	11,406.5
Mg	1,080.8	1,445
SO_4^{2-} - S	**39.91**	**69.24**
Fe	285.76	23.37
Zn	0.03	0.05
Cu	0.07	0.01
Mn	4.56	5.26
pH	5.7	6.5

ANAEROBIC MICROCOSM EXPERIMENTS



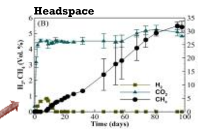
Nutrient solution

Compound	Amount /120 ml
Resazurin	100 µL
$Na_2S \cdot 9H_2O$	0.1 g
$NaHCO_3$	1.2 g
$Na_2MoO_4 \cdot H_2O$	0.01 g
Crude oil	1 ml
Protein-rich matter	0.24 g

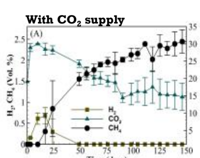
(a) Anaerobic chamber
(b) Microcosms kept in the incubator at 50 °C
(c) Gas chromatography analysis: headspace and remaining crude oil

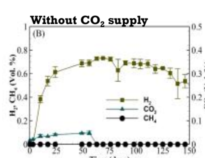
STIMULATING EFFECT OF CO2 AND PROTEIN-RICH MATTER ON METHANOGENIC CRUDE OIL BIODEGRADATION

- The combined supply of CO_2 and protein-rich matter stimulates:
  - H_2 formation
  - Methanogenesis
  - Crude oil biodegradation



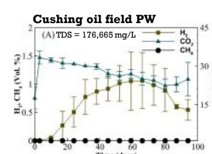
RELEVANCE OF CO_2 SUPPLY IN STIMULATING METHANOGENESIS

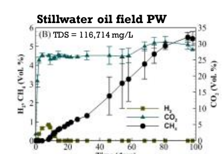




- CH_4 production only occurred in the microcosm supplied with CO_2 as $NaHCO_3$

RELEVANCE OF THE CHEMICAL COMPOSITION OF PRODUCED WATER (PW)

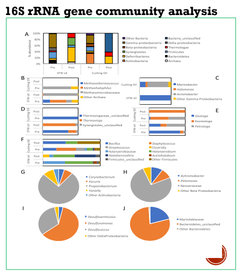




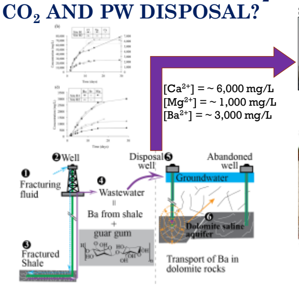
- Although H_2 accumulation with PW from the Cushing oil field did occur, this did not result in the production of CH_4

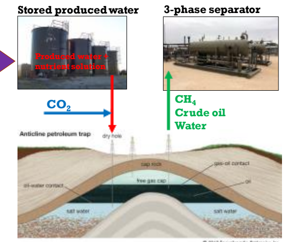
MECHANISM OF METHANOGENIC CRUDE OIL BIODEGRADATION STIMULATION

- The combined supply of protein-rich matter and CO_2 promotes the syntrophic growth of a crude oil-degrading microbial community
- High salinity (TDS) levels inhibits the syntrophic growth of a crude oil-degrading microbial community
  - The growth of methanogenic microbes was not possible in PW from the Cushing oil field (TDS = 176,665 mg/L).



BENEFICIAL USE OF CO_2 AND PW: COUPLING OF CO_2 AND PW DISPOSAL?





a) Mineral trapping of CO_2 and heavy metals
b) Biogenic recycling of CO_2 to CH_4
c) Enhanced hydrocarbon recovery

CONCLUSIONS

- Ba mobility is higher in deep saline aquifers than in shallow freshwater aquifers
- PW contains indigenous methanogenic microbial communities that could be used to recover crude oil in the form of CH_4
  - The combined supply of protein-rich matter and CO_2 stimulates methanogenesis from crude oil and CO_2
- Coupling of CO_2 and PW disposal into depleted oil reservoirs by the proposed method constitutes an alternative to
  - Biogenically recycle CO_2 to CH_4
  - Enhance the recovery of crude oil
  - Trap CO_2 and heavy metals as carbonate minerals

QUESTIONS?

ACKNOWLEDGEMENTS

- Microbial diversity analysis
  - Drs. Mostafa Elshahed and Noha Youssef
- Produced water and crude oil samples collection
  - Dr. James Puckette
  - Mr. Toby Williams (Glimp Oil Co.)
- Crude oil analysis
  - Dr. Tao Wu

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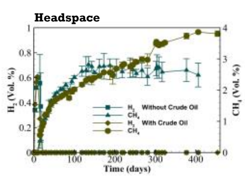
STIMULATION OF METHANOGENIC CRUDE OIL BIODEGRADATION

- If CH_4 was produced only from the biodegradation of the supplied protein-rich matter, CH_4 production in both microcosms – with and without the crude oil supply – would have been the same (4.0 Vol. %).



Comparison of H_2 and CH_4 gas production in the headspace of microcosms with (1 mL) and without crude oil supply. Both microcosms were supplied with protein-rich matter (2 g/L)