SULFIDE EFFECT ON BIOGAS UPGRADING WITH A BIOELECTROCHEMICAL SYSTEM

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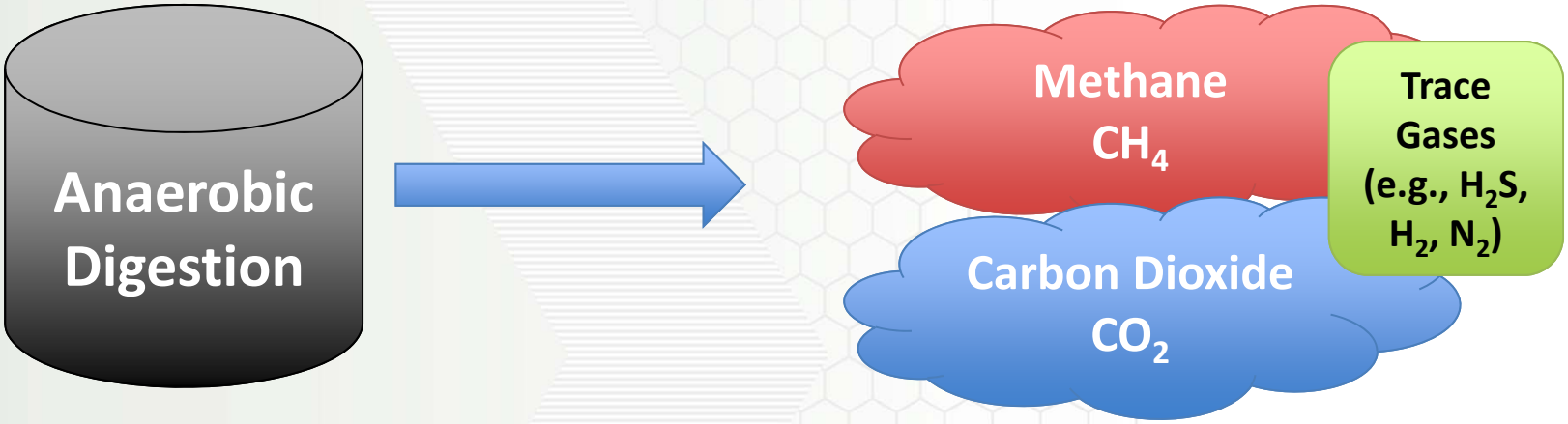
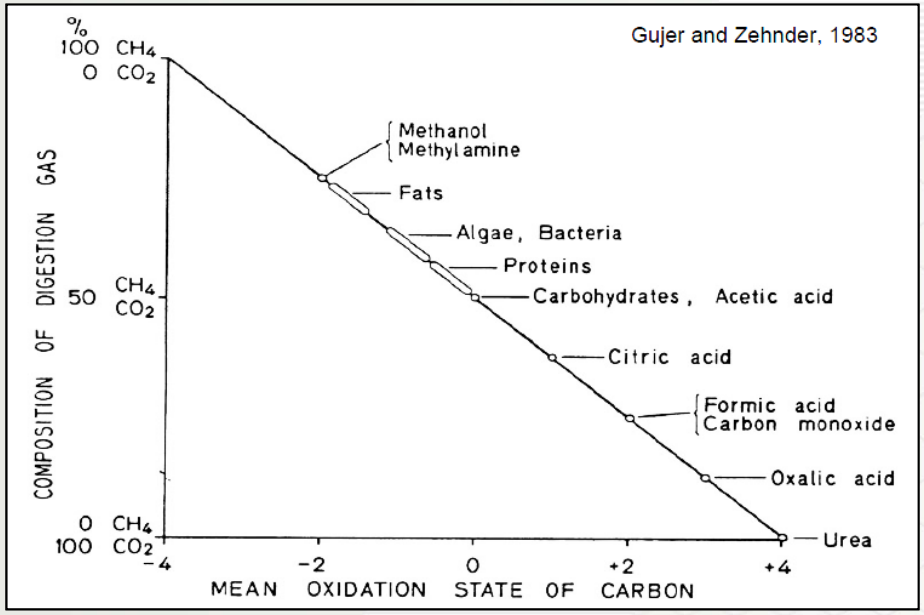
CREATING THE NEXT

INTRODUCTION & BACKGROUND





Substrate	Biogas Yield (L/kg volatile solids)[a]	Methane Content (%, v/v)
Fat	1,000 – 1,250	70 – 75
Protein	600 – 700	68 – 73
Carbohydrate	700 – 800	50 – 55

[a] At 25°C, 1 atm; Petersson and Wellinger, 2009. *IEA Bioenergy*.

BIOGAS UPGRADING

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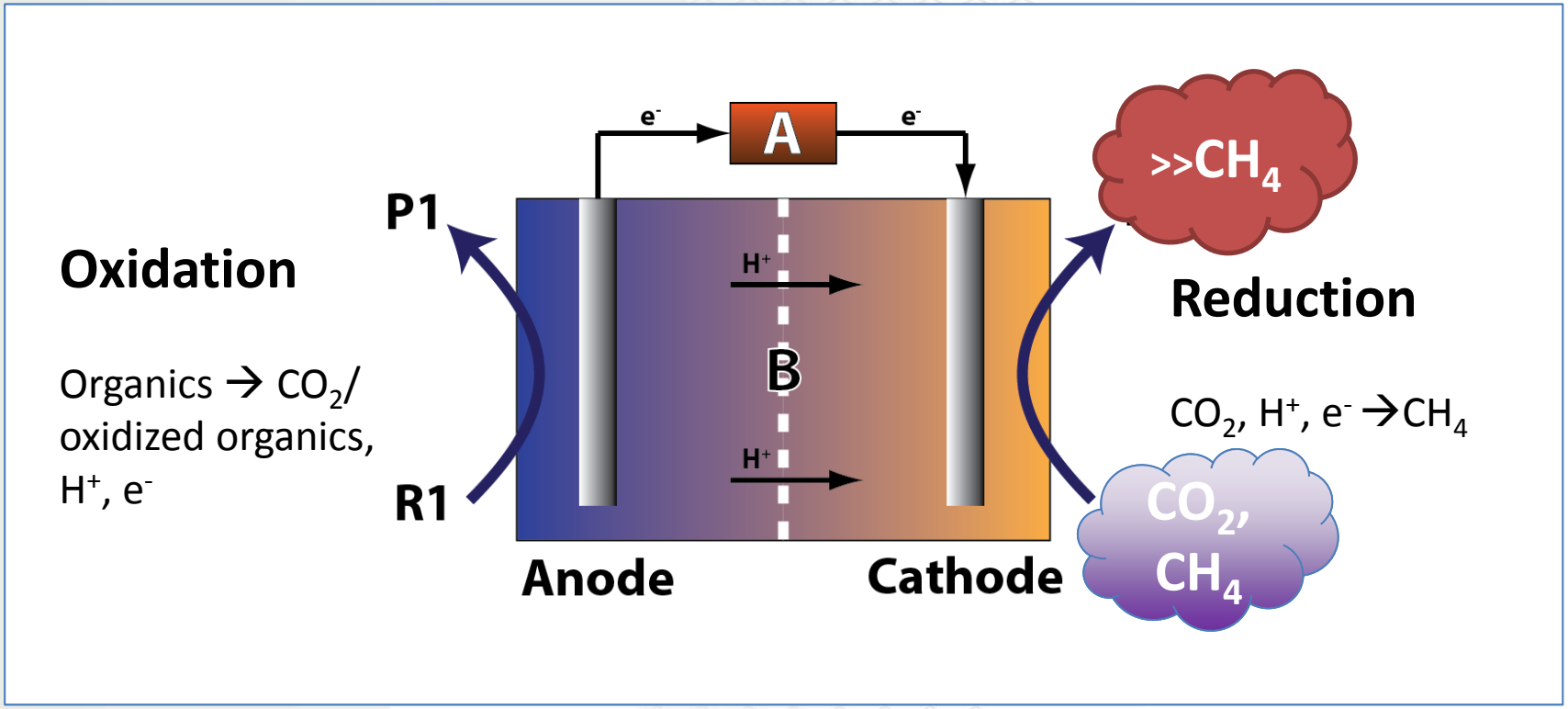
- Biogas Upgrading
  - Absorption
    - Physical
    - Chemical
  - Adsorption
    - Activated Carbon
    - Alumina
    - Zeolite
  - Membranes
    - Gas separation
    - Gas adsorption
  - Cryogenics
  - Biological
    - Biomass Production (e.g., algae)
    - **Bioelectrochemical Systems**

- *Energy intensive*
- *Carbon waste product*
- *Expensive consumables*

Direct conversion of CO_2 to CH_4

BIOELECTROCHEMICAL SYSTEMS

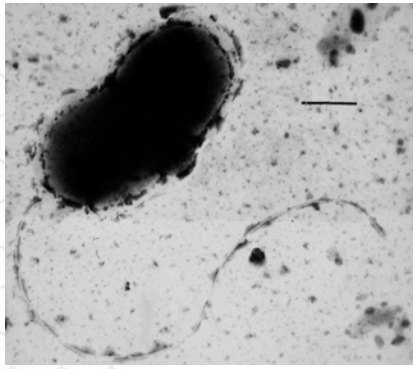


- Microbes are an inexpensive, self-renewing catalyst
- The potential applied at A (< 1 V) can be supplied by photovoltaics/renewables
- Optional proton exchange membrane, B

HYDROGEN SULFIDE

- Corrosive, toxic (NIOSH, IDLH = 100 ppm)
- Produced by sulfate-reducing bacteria during anaerobic digestion
- Inhibitory to methanogenesis during anaerobic digestion [1]
- Feedstock C:S ratio predicts biogas H_2S [2]

Feedstock	C/S (g/g)	Theoretical Biogas H_2S (%, range)
Grease trap waste	798	0.0 – 0.1
Biological sludge	59	0.6 – 1.9
Industrial WW biological sludge	46	0.8 – 2.0
Pig bristles	19	2.0 – 4.9
Harvested green seaweed	7	5.5 – 17.7



Desulfovibrio vulgaris

[1] Chen, Y., et al., 2008. Biores. Technol. 99(10), 4044-4064.

[2] Peu, P., et al., 2012. Bioresource Technol. 121, 419-424.

RESEARCH OBJECTIVE

Determine how the presence of hydrogen sulfide (H_2S), a common contaminant in anaerobic digester biogas, affects the conversion of carbon dioxide (CO_2) to methane (CH_4) in the cathode of a bioelectrochemical system (BES).

RESEARCH APPROACH

- Compare the mean initial 3-day CH_4 production rate following feeding
- Assess the effect of H_2S on the full BES performance

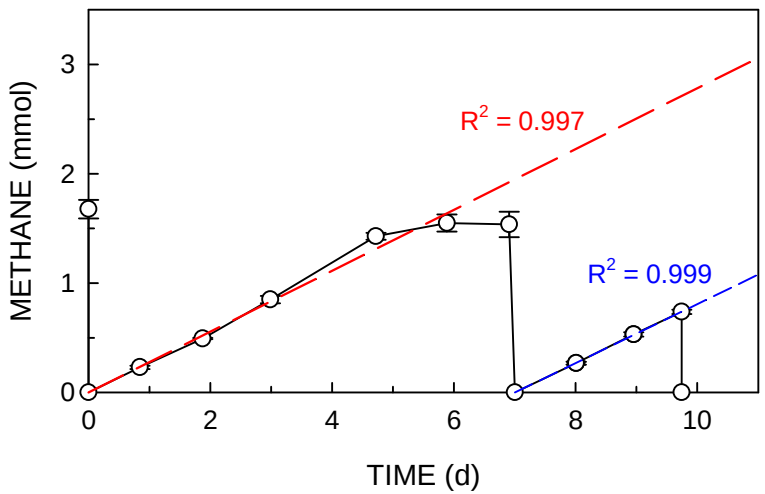
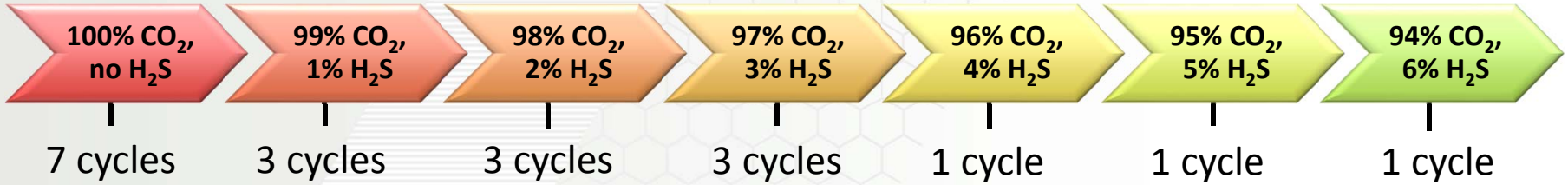


Figure 1. Linear biocathode CH_4 production during the first 3 days of a feeding cycle



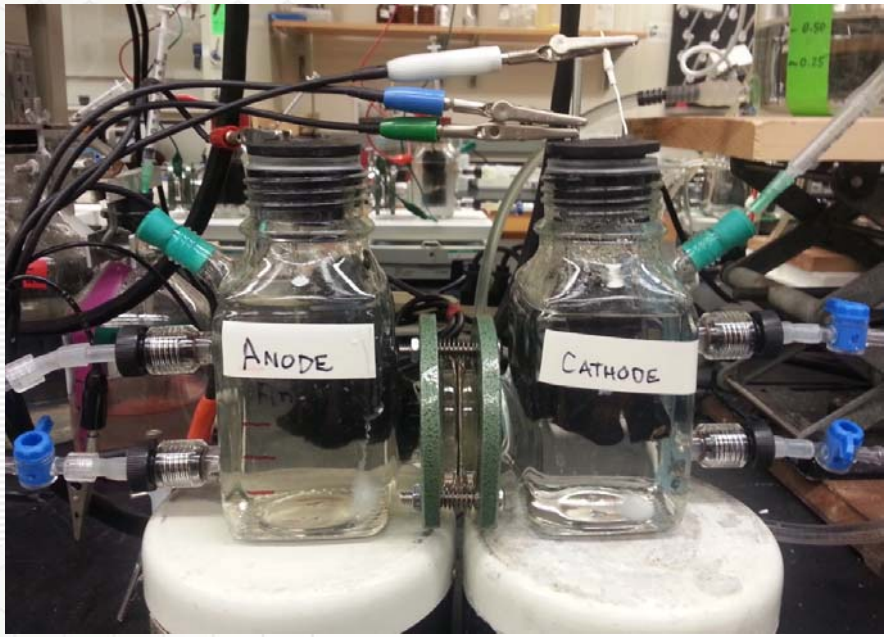
METHODS: BIOELECTROCHEMICAL SYSTEM

Anode

- 300 mL total, 250 mL liquid volume
- Carbon felt electrode with exoelectrogens
- Batch-fed acetate (4 g COD/L) weekly

Cathode

- 300 mL total, 250 mL liquid volume
- Carbon felt electrode with methanogens and SS collector
- Batch-fed $CO_{2\ (g)}$ (92 mL at 22°C, 1 atm) weekly
- Applied potential -0.8 V vs. SHE with Gamry Interface 1000 potentiostat



- Continuously mixed with magnetic bars and stir plates at 22°C
- Nafion 117 proton exchange membrane (PEM)

RESULTS: BIOCATHODE CH_4 PRODUCTION

- H_2S improves biocathode CH_4 production rate up to 2-3% initial H_2S
- Initial H_2S concentrations of 4-6% result in a decreased biocathode CH_4 production rate
- **<u>Two competing effects</u>:**
  - **Depress CH_4 production (≥4% H_2S):** Inhibition of methanogens?
  - **Improve CH_4 production (≤3% H_2S):** What is/are the process(es) involved?

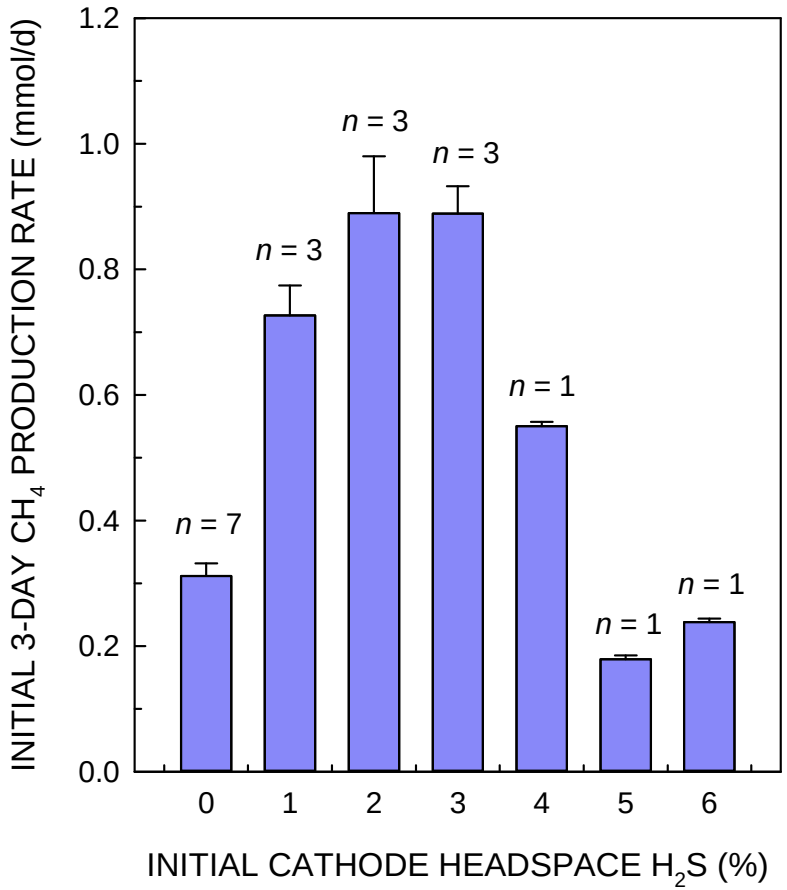
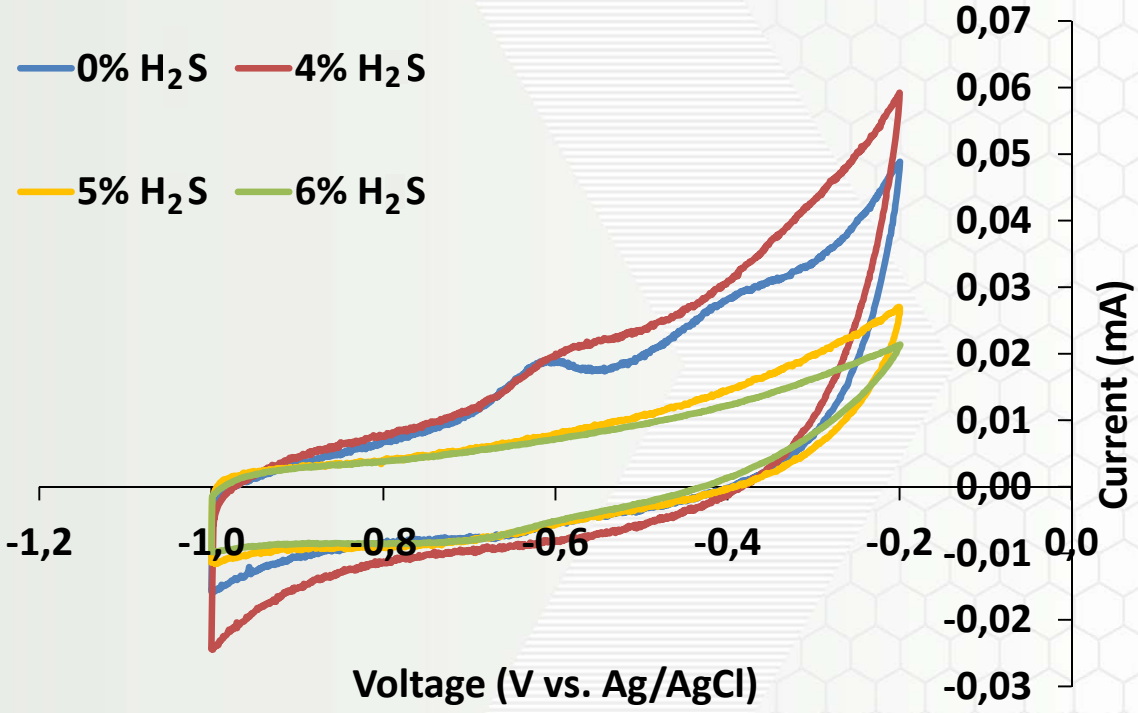


Figure 2. Mean initial 3-day biocathode CH_4 production rates following feeding with an initial headspace concentration of 0-6% H_2S (*n*, number of feeding cycles).

ELECTROCHEMICAL PERFORMANCE



H_2S (%)	CE (%)	CCE (%)
0	11	100
4	19	99
5	58	13
6	58	15

CE, Coulombic Efficiency: The ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removal produced current. [1]

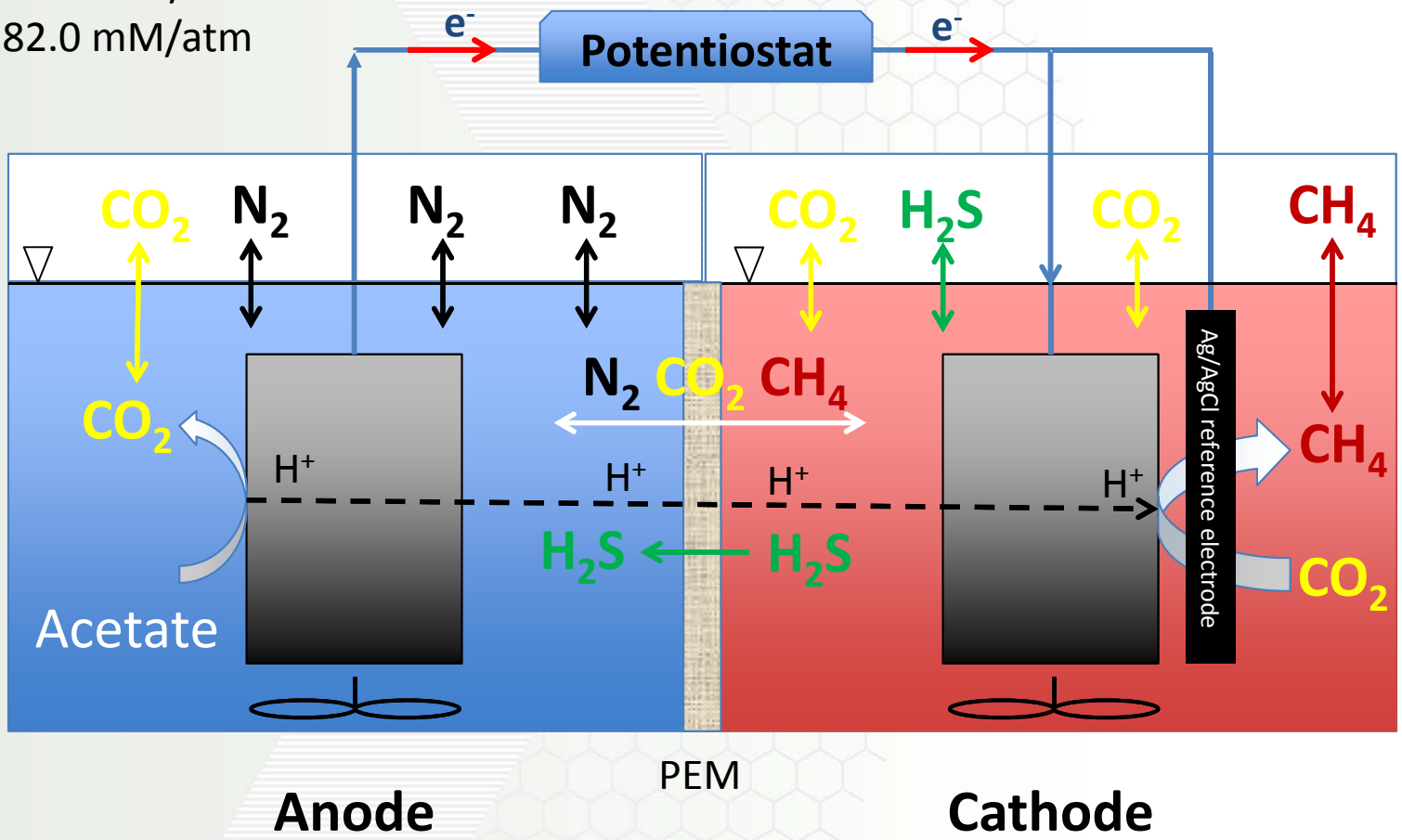
CCE, Cathode Capture Efficiency: The ratio of total Coulombs actually transferred to the CH_4 from the cathode, to maximum possible Coulombs if all current produced CH_4. [2]

[1] Logan et al., 2006. ES&T
[2] Villano et al., 2013. Bioresource Technol.

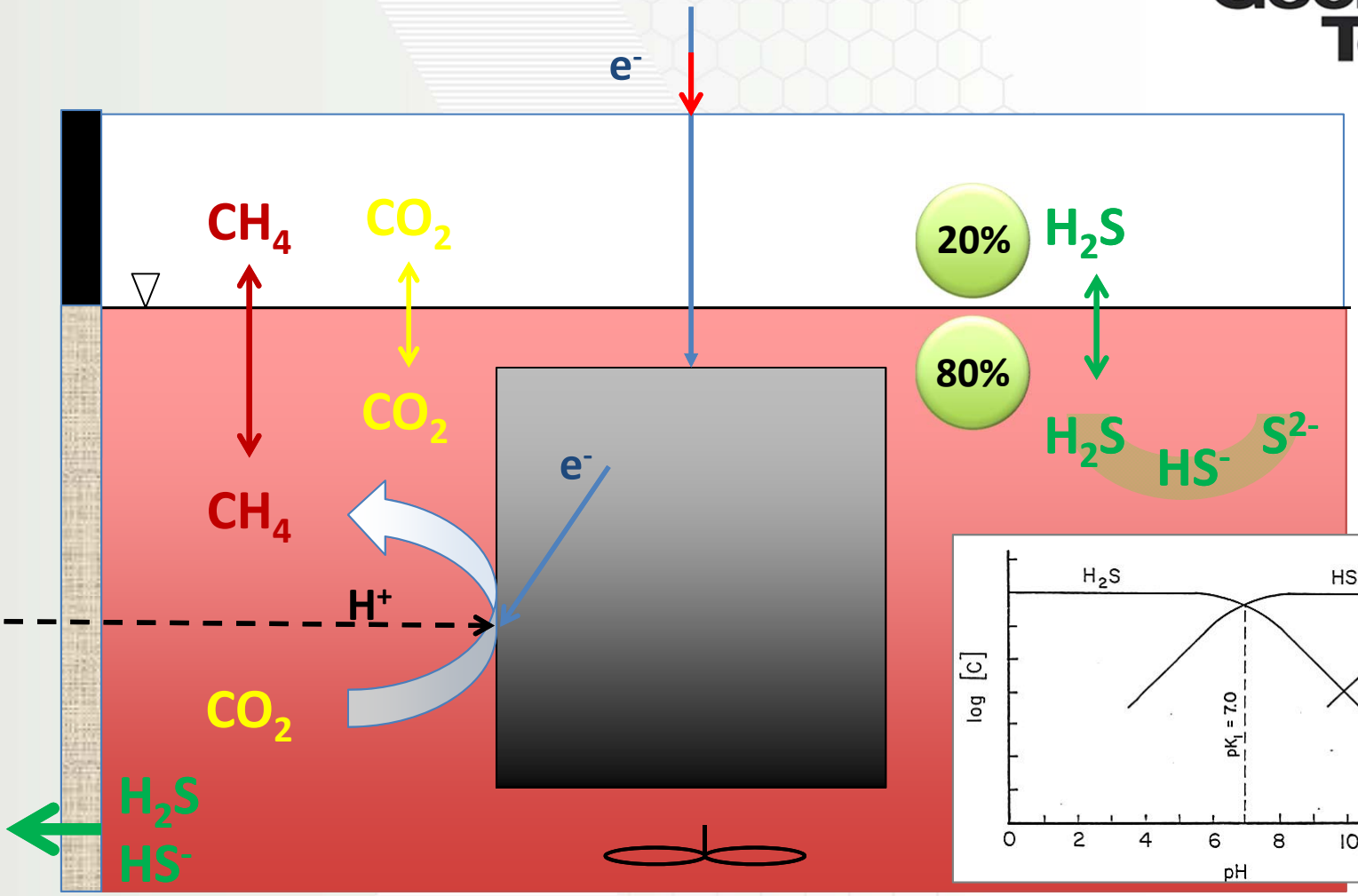
H_2S WITHIN A METHANOGENIC BES

Henry's Law constant in catholyte medium

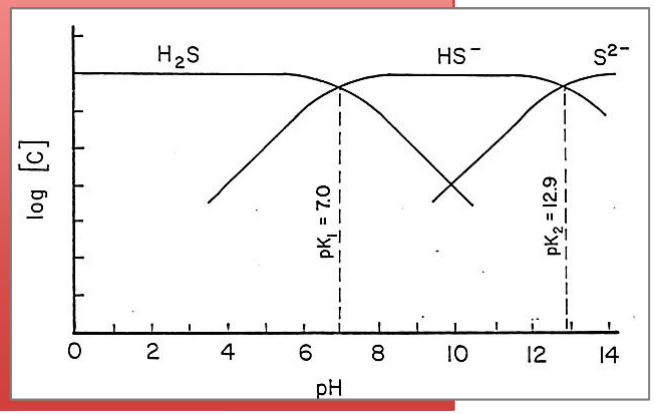
- CO_2: 32.7 mM/atm
- H_2S: 82.0 mM/atm



H_2S IN THE CATHODE – INHIBITORY EFFECT



H_2S is the most toxic of the sulfide species



H_2S IN THE CATHODE – INHIBITORY EFFECT

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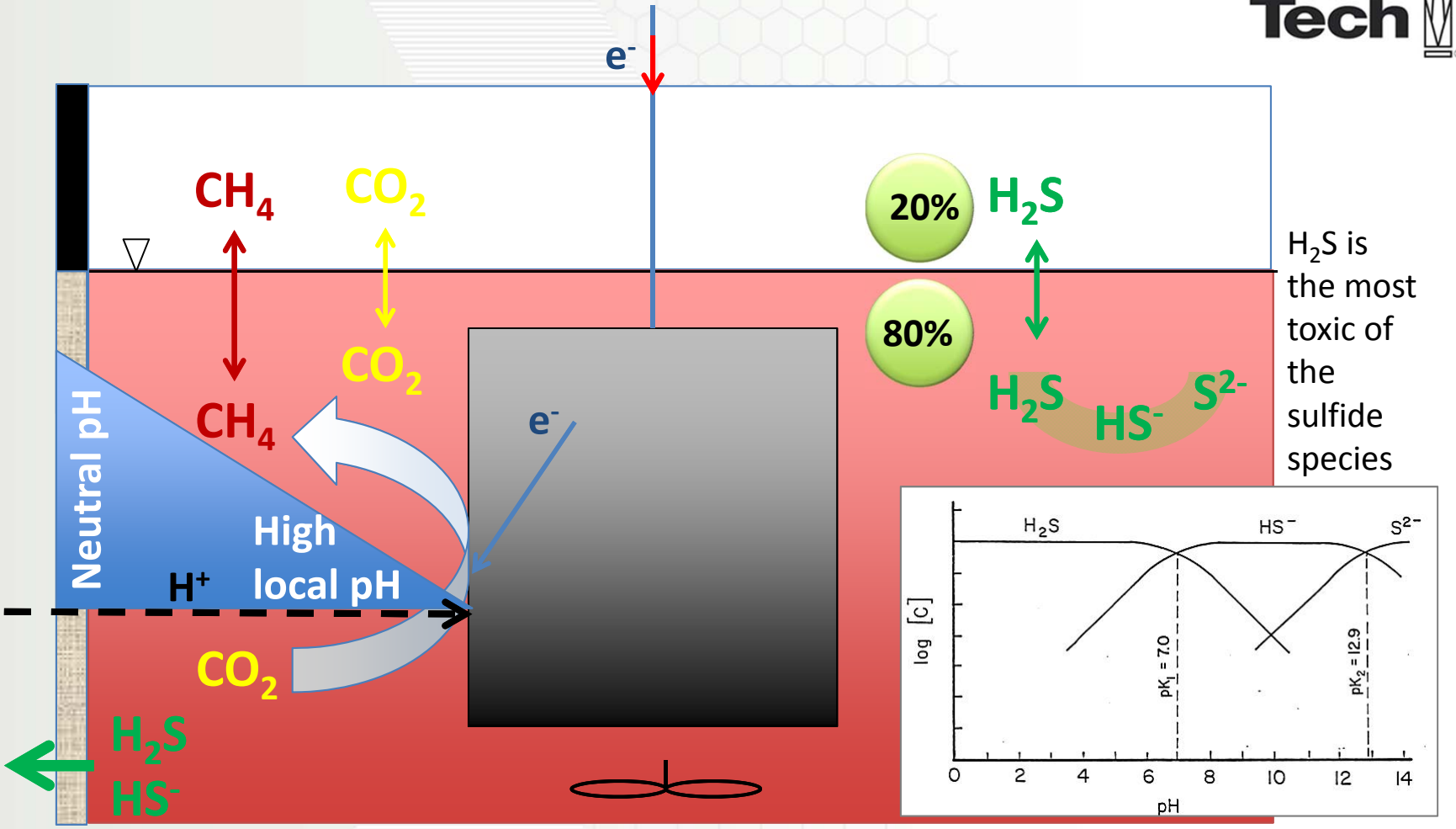
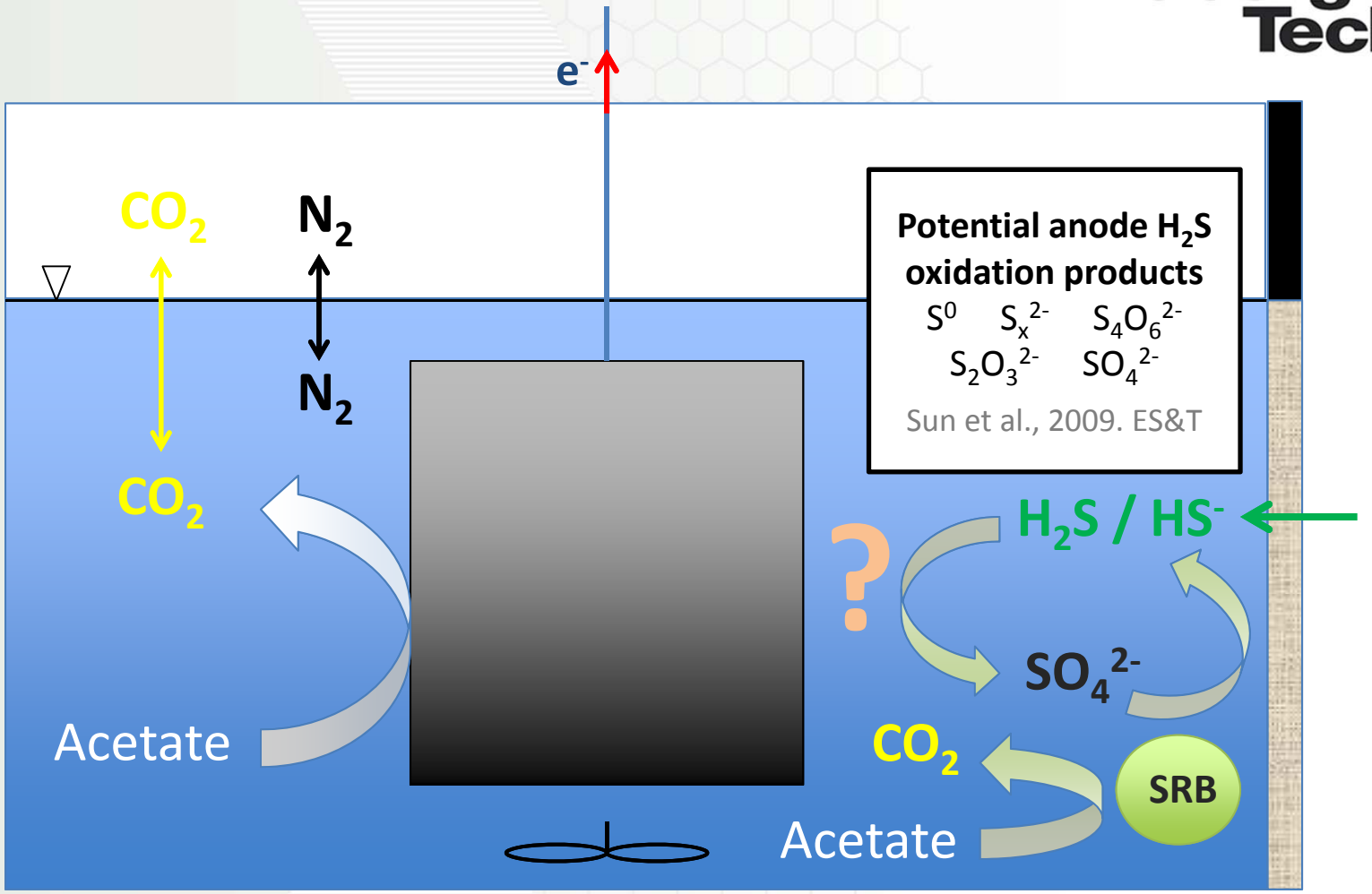


H_2S is the most toxic of the sulfide species

The methanogenic biocathode is semi-protected from sulfide inhibition by **biofilm formation** and a **local high pH** at the cathode surface.

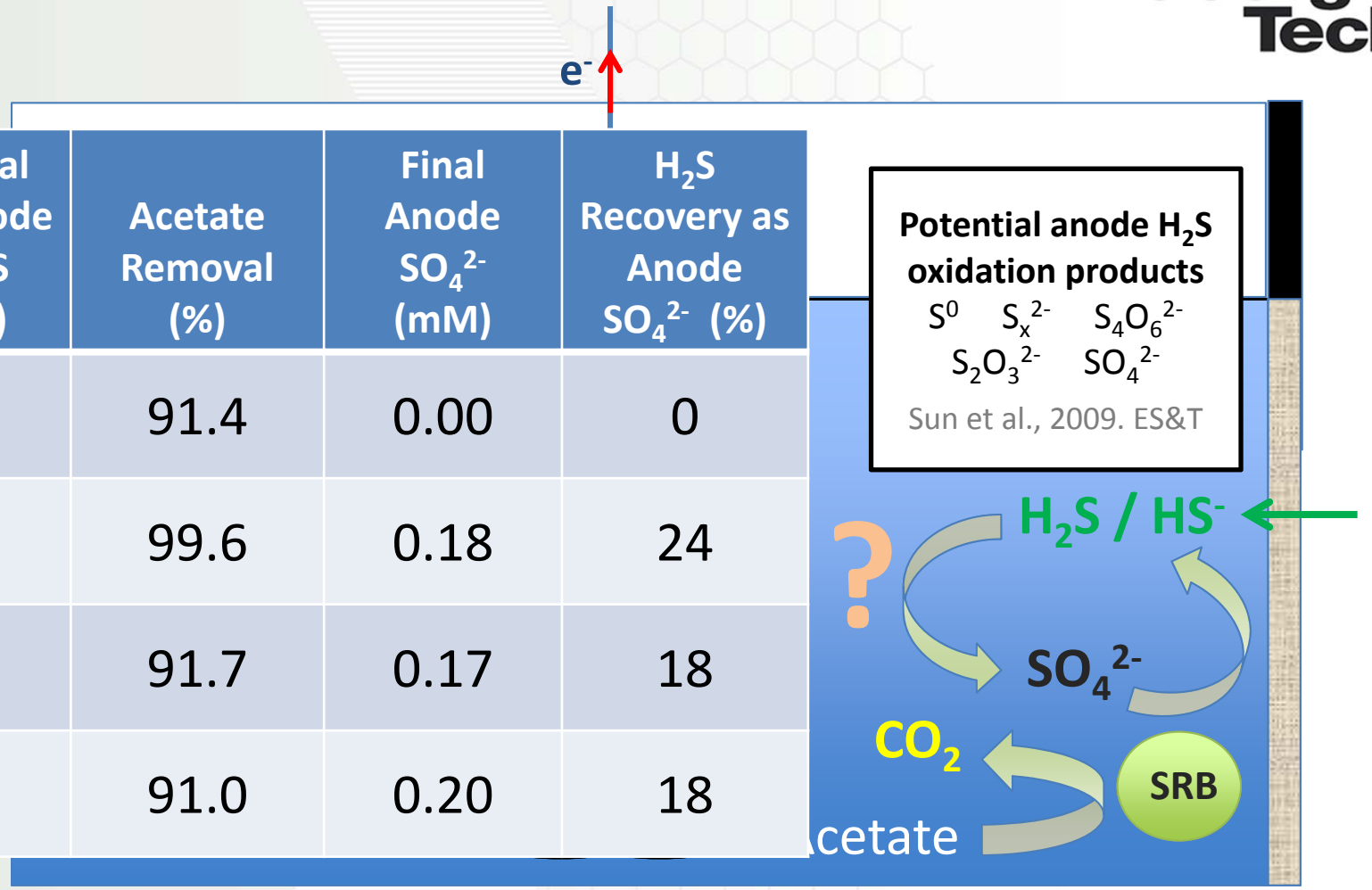
H_2S IN THE ANODE – ENHANCEMENT EFFECT



- Low H_2S → more electrons donated to the anode → more biocathode CH_4 production
- High H_2S → stimulate SRB cycle → divert acetate eeq from the anode → less biocathode CH_4 production

H_2S IN THE ANODE – ENHANCEMENT EFFECT

Initial Cathode H_2S (%)	Acetate Removal (%)	Final Anode SO_4^{2-} (mM)	H_2S Recovery as Anode SO_4^{2-} (%)
0	91.4	0.00	0
4	99.6	0.18	24
5	91.7	0.17	18
6	91.0	0.20	18



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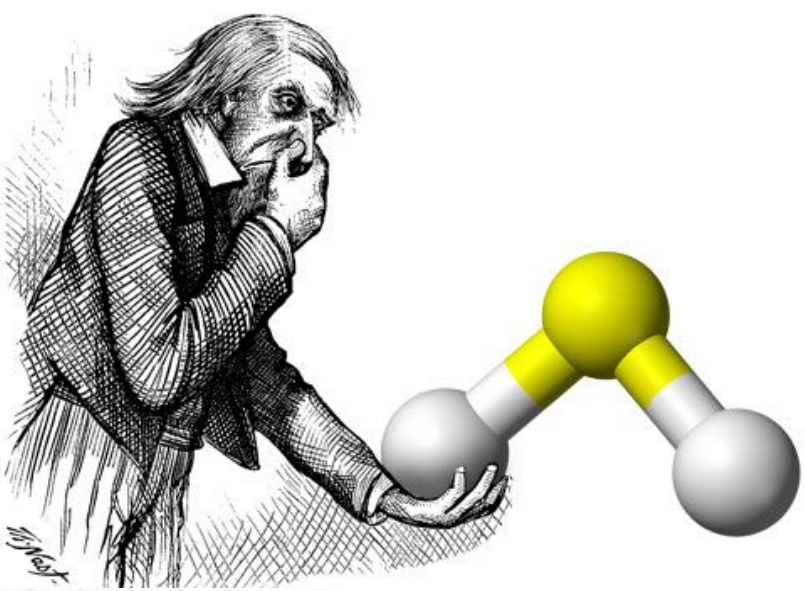
BIOCATHODE H_2S REMOVAL

Initial Cathode H_2S (%)	Acetate Removal (%)	Final Anode SO_4^{2-} (mM)	H_2S Recovery as Anode SO_4^{2-} (%)	Final H_2S in Catholyte (mM)	Final H_2S in Cathode Gas (%)	H_2S Removal Efficiency (%)
0	91.4	-	-	-	-	-
4	99.6	0.18	24	0.47	0.5	84.6
5	91.7	0.17	18	0.63	0.7	83.4
6	91.0	0.20	18	0.81	1.0	83.2

CONCLUSIONS

- Up to 3-4% H_2S in biogas can **enhance** biocathode CH_4 production by **contributing electrons to the anode**
- Above 4% H_2S, biocathode CH_4 production **decreases** due to: **i) inhibition** of methanogens at the cathode; **ii) sulfide oxidation cycling** in the anode, which diverts electron equivalents away from CH_4 production



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METHODS: ANALYTICAL

- Gas pressure → Pressure transducer
- Gas composition → Gas chromatography (GC) with Thermal Conductivity Detector (TCD)
- Acetate → GC with Flame Ionization Detector (FID)
- Dissolved CO_2, H_2S → Sample acidification (6 N H_2SO_4) followed by composition analysis of evolved gas (conditional calibration)
- Voltage
- Current
- Cyclic Voltammetry

→ Handheld multimeter and Gamry Interface 1000 potentiostat

RESULTS: SERUM BOTTLE TESTS

- Cathode inoculum: hydrogenotrophic, methanogenic, suspended growth culture fed with H_2/CO_2 (80:20) and catholyte medium with vitamins and trace metals
- Similar methane production at all initial gaseous H_2S concentrations up to 3% H_2S