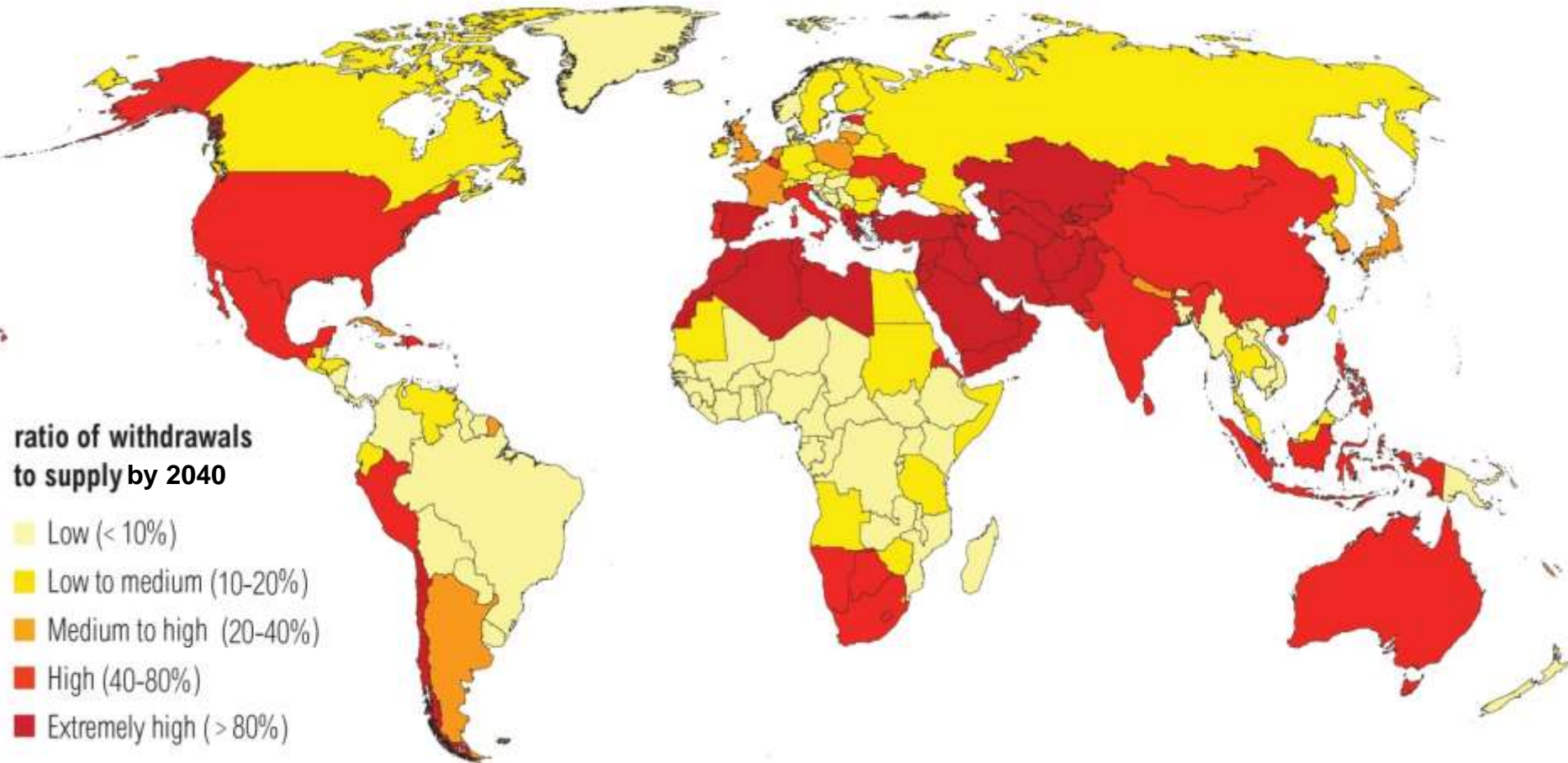




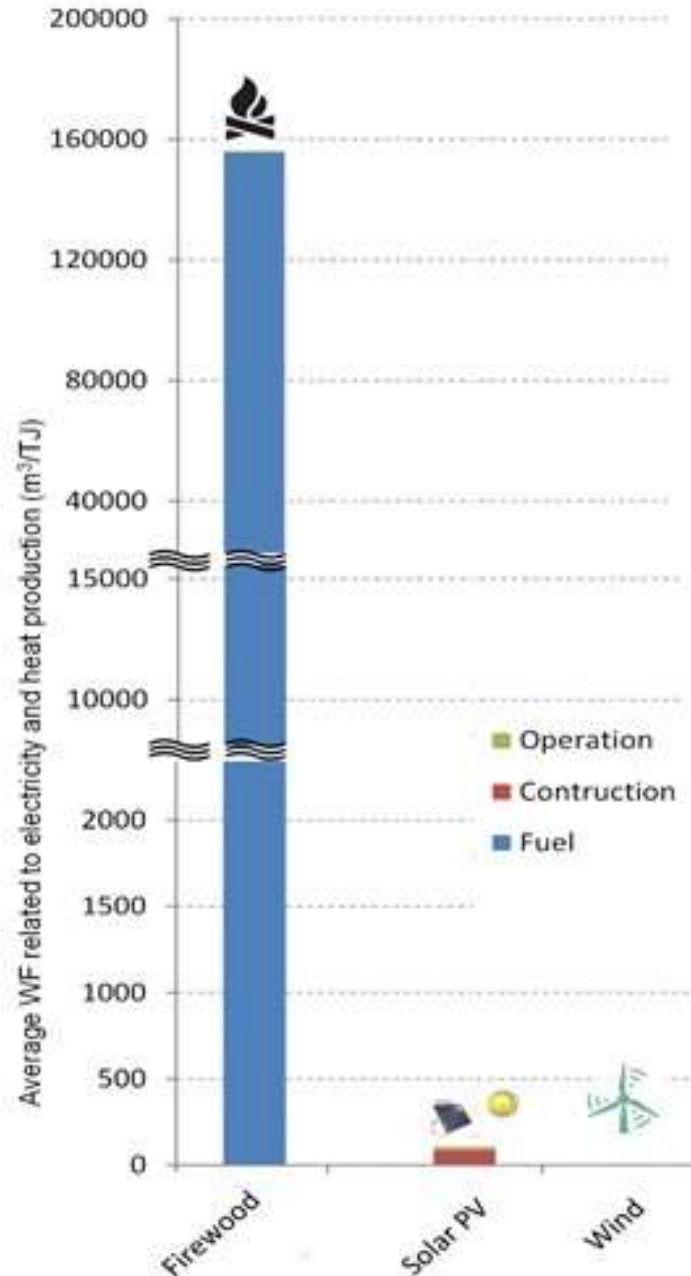
# Recovery of CSNP

**prof.dr.ir. Cees J.N. Buisman**  
Wageningen 9 november 2017

# Water Scarcity limits biobased economy



# Biomass production is very water intensive



# Carbon source for Renewable chemicals

- Biowaste

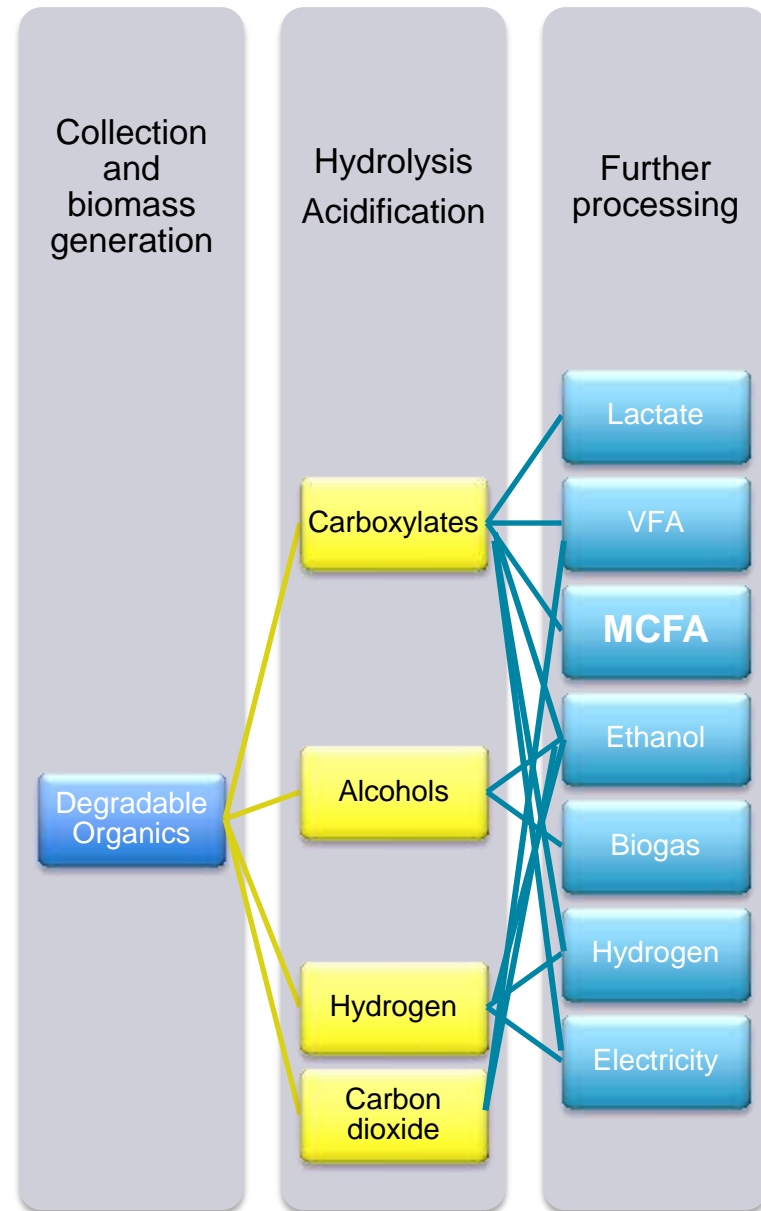
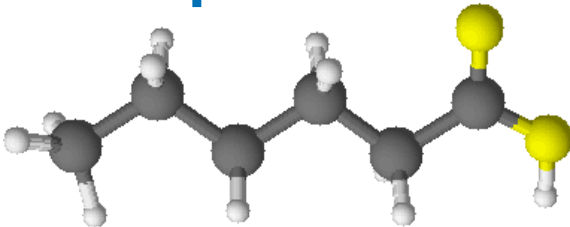


# Carboxylate platform

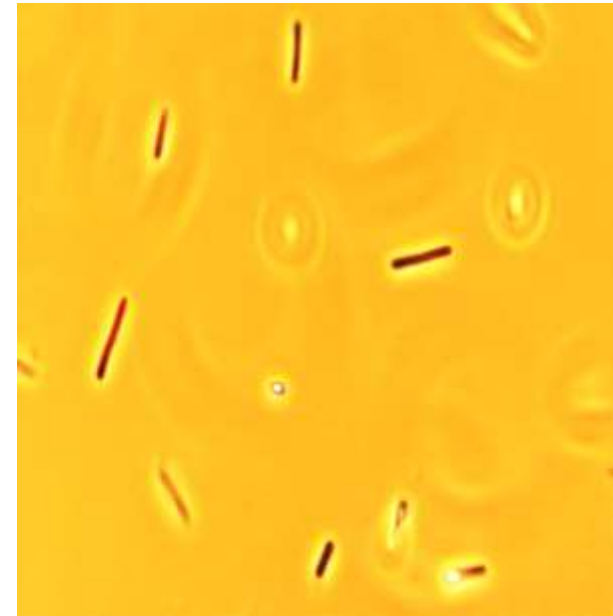
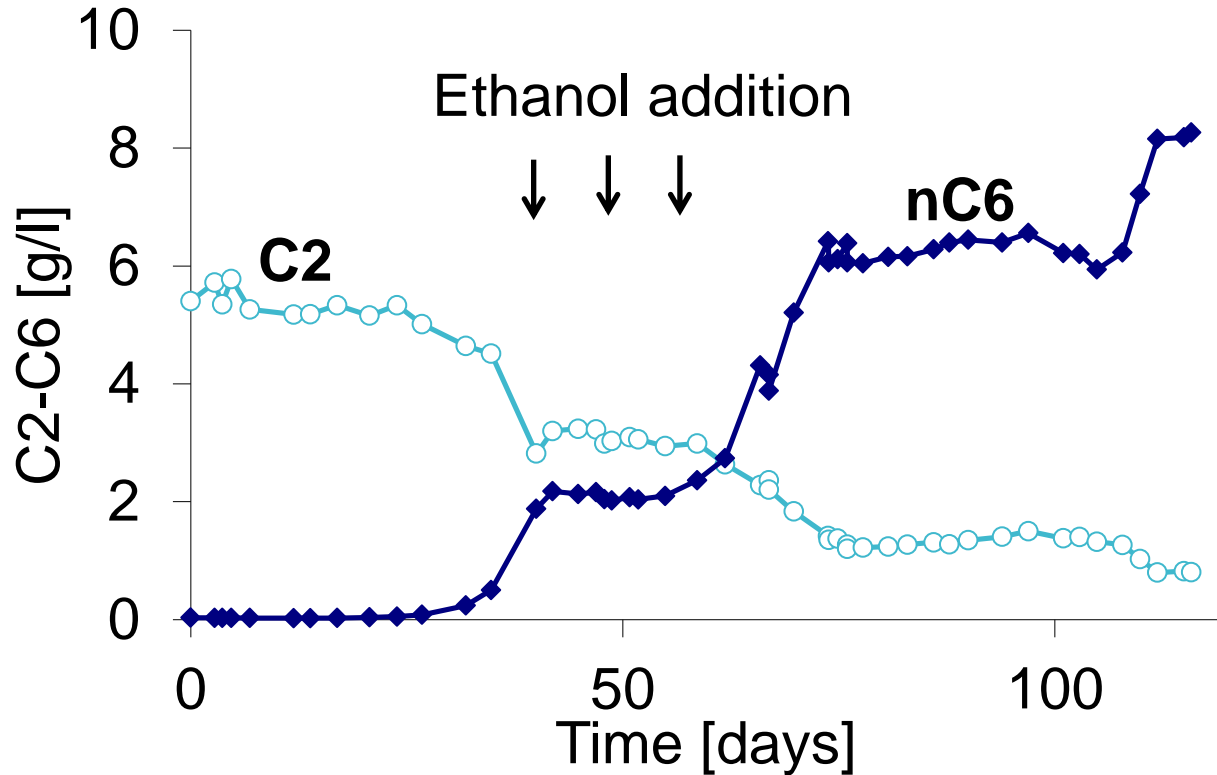
- Alcohols
- Carboxylates
- Hydrogen, Biogas
- Electricity

## Focus:

### Caproic acid



# Proof-of-principle of open culture chain elongation of acetate to caproic acid (C6)



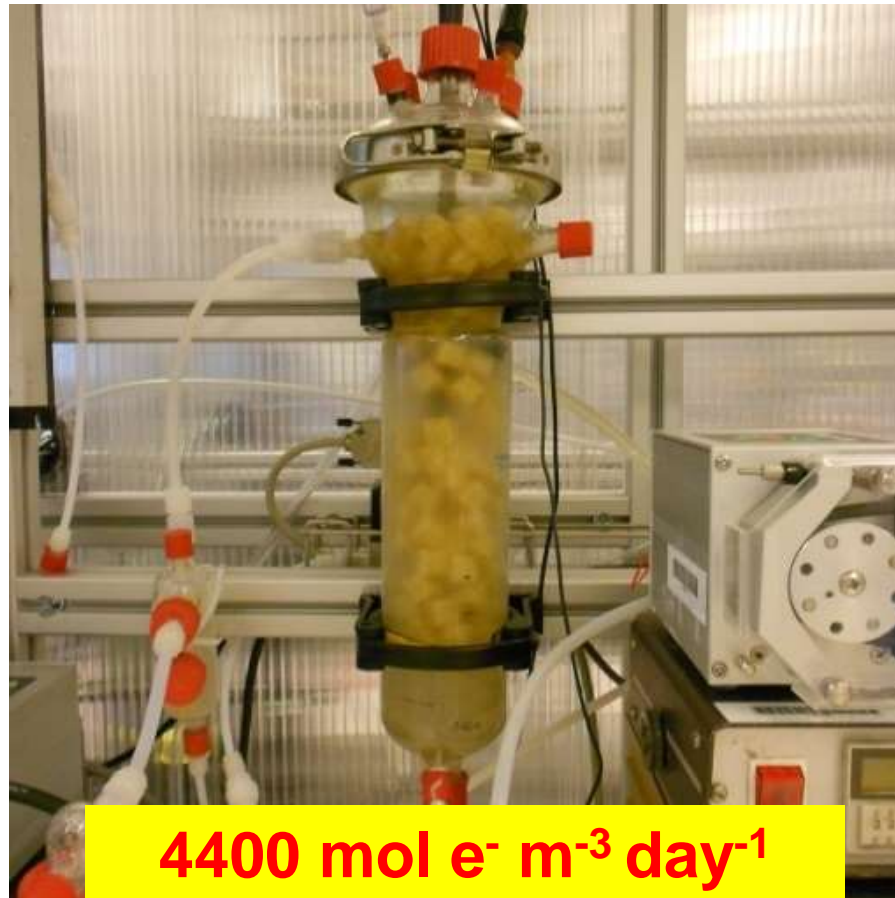
*Clostridium kluyveri*

VPR C6  $0.45 \text{ g.l}^{-1}.\text{d}^{-1}$

Steinbusch K.J.J., 2010, PhD thesis, Liquid biofuel production  
Steinbusch K.J.J et al. 2011. EES 4, 216-224.

# World record on caproate (C6) production at 57 g/l/d with short HRT and high loads

MCFA  
selectivity 81%



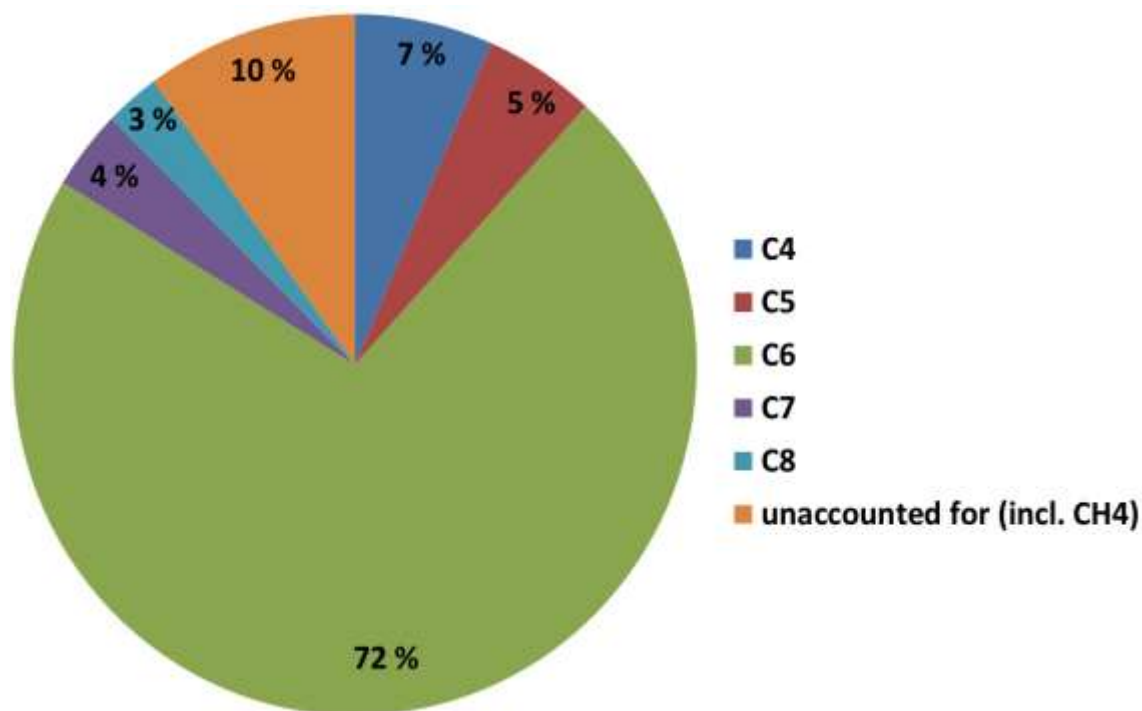
Grootscholten *et al.* BRT 136 (2013) 735–738

# Two-stage MCFA production from real municipal solid waste and ethanol

MCFA selectivity 83%

VPR 28.1 g.l<sup>-1</sup>.d<sup>-1</sup>

Caproate 12.6 g l<sup>-1</sup> > solubility caproic acid in water

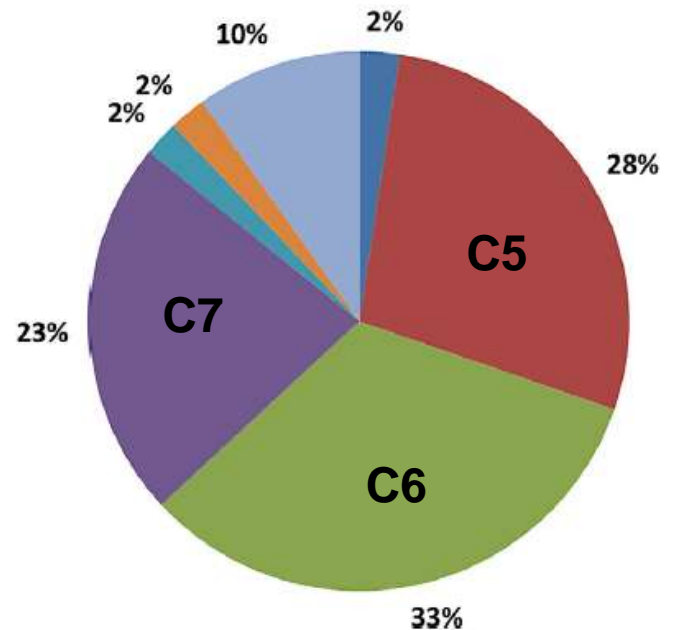
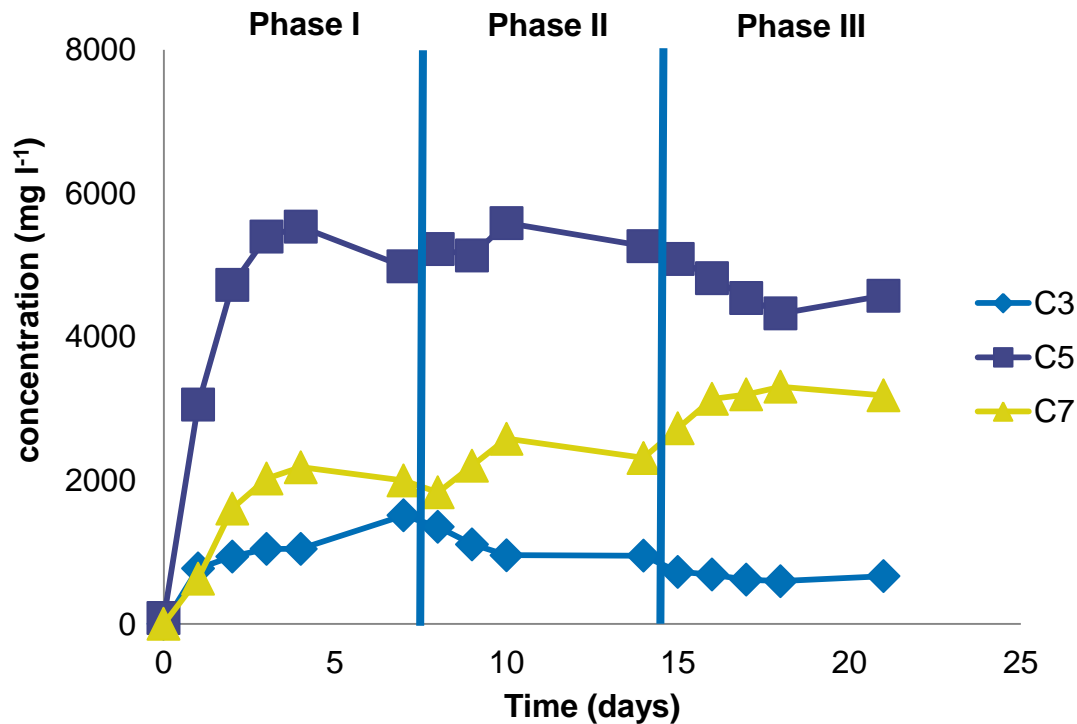




# Heptanoate (C7) production by chain elongation of propionate

C7 selectivity 23%

Heptanoate 4.5 g.l<sup>-1</sup>.d<sup>-1</sup>



# Upscaling



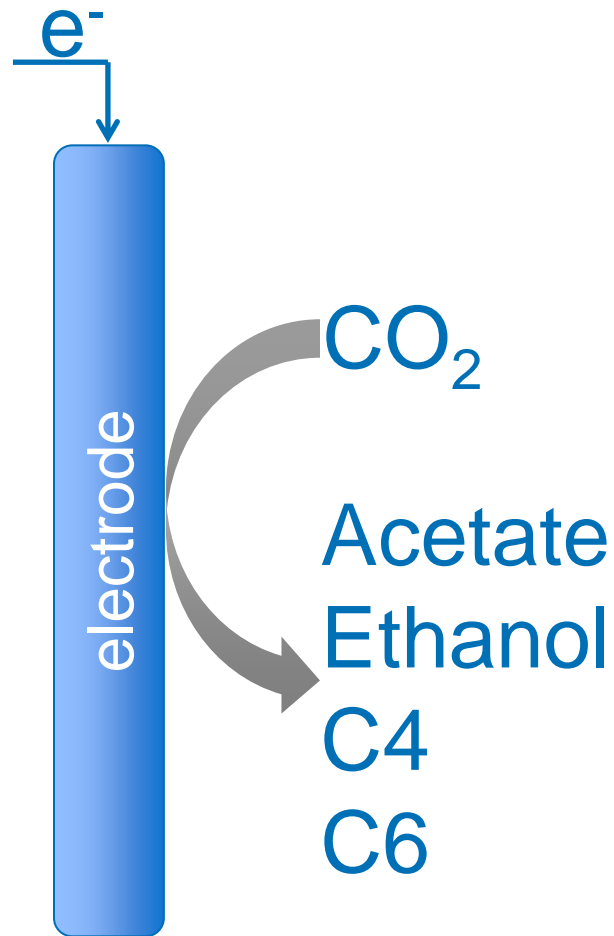
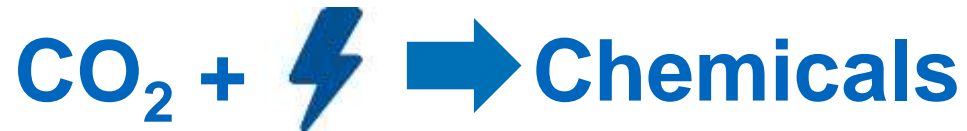
Lab  
~0.3 kg/d



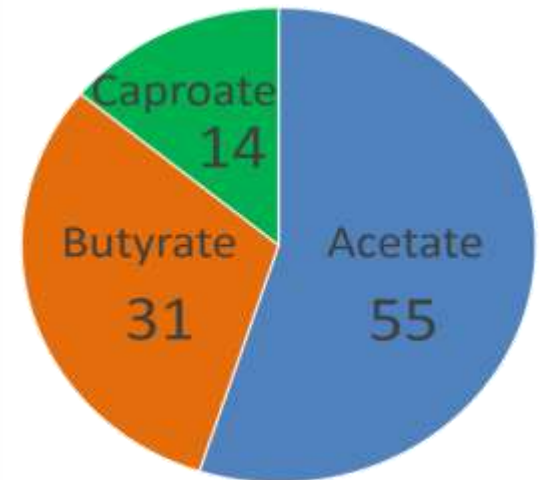
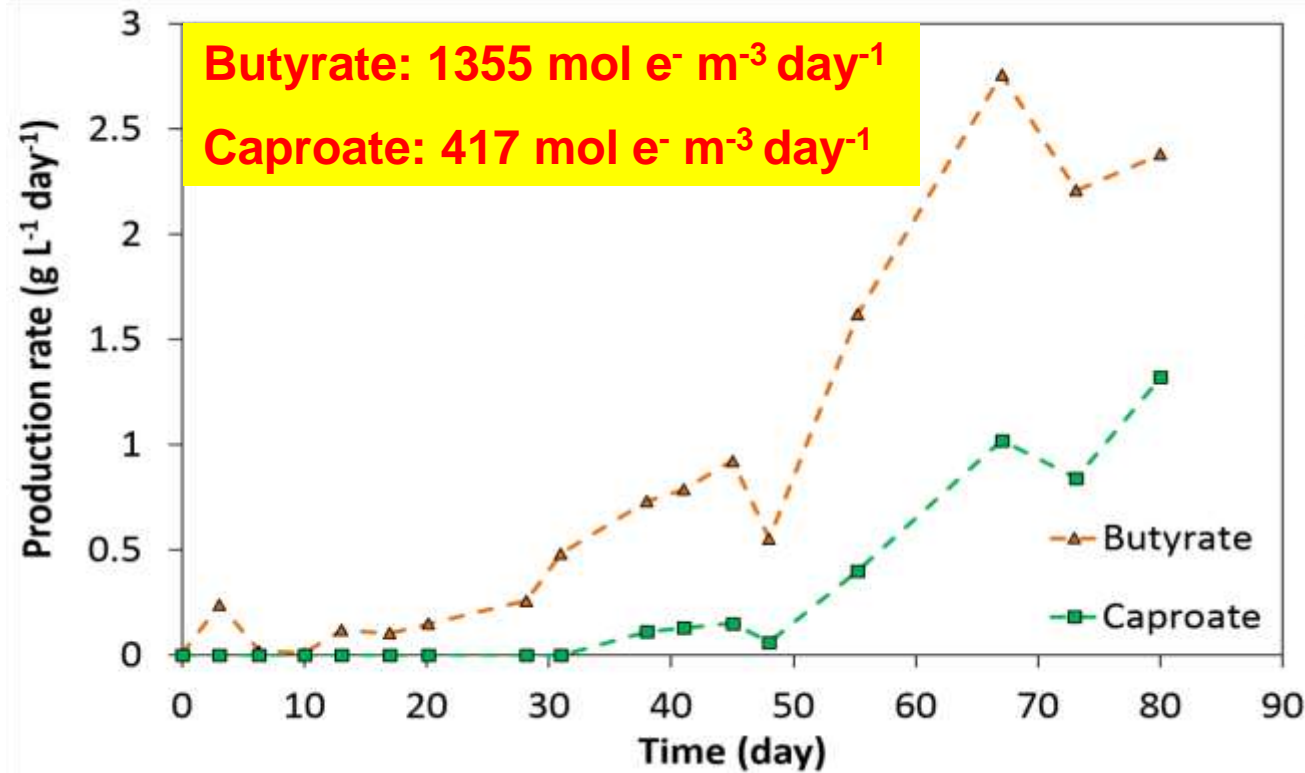
Pilot  
~3 kg/d



Full-scale  
~3 ton/d



# Bioelectrochemical caproate production without added mediator

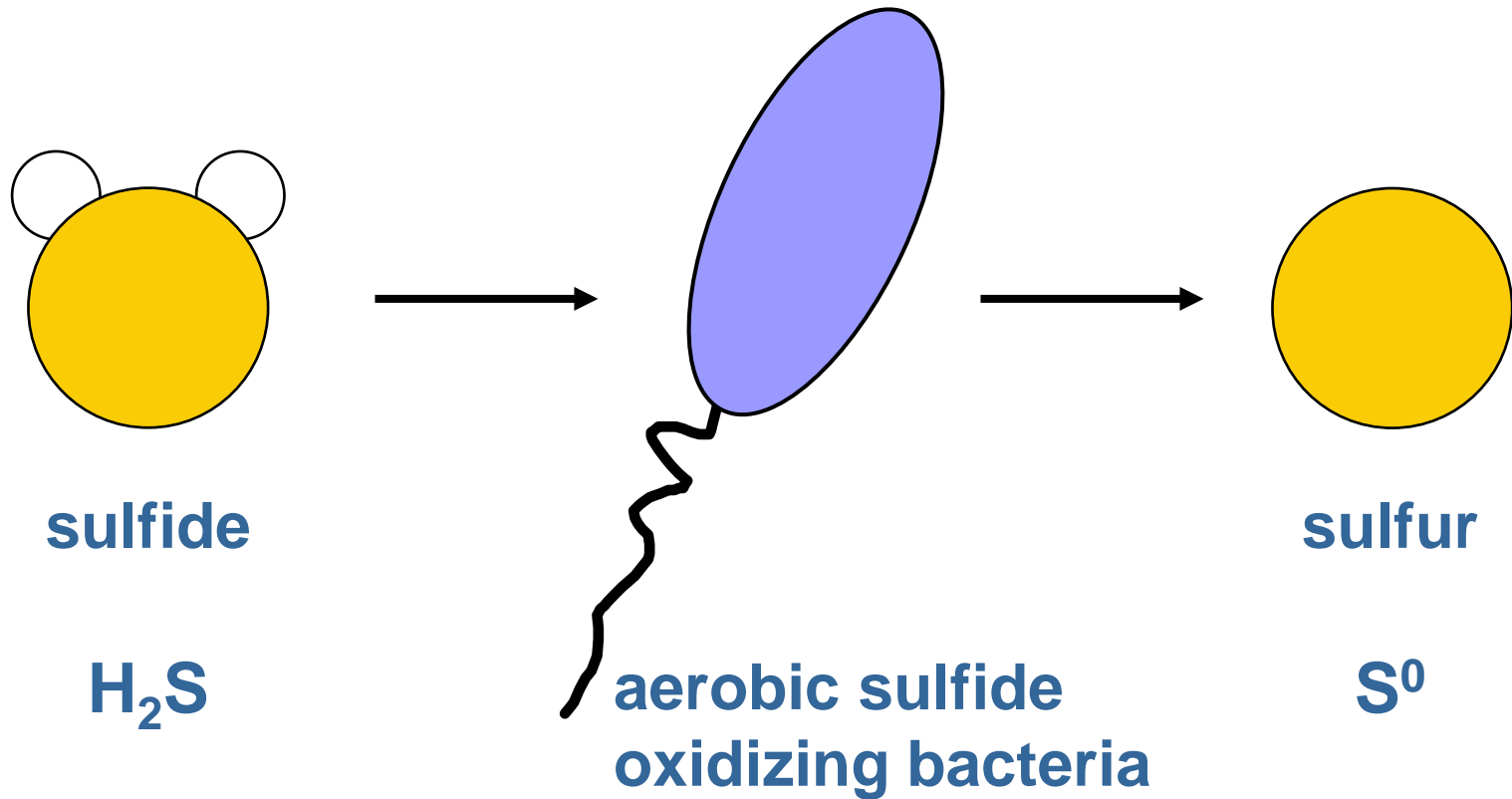


Jourdin, L., Raes, S. M. T., Buisman, C.J.N., Strik, D.P.B.T.B. Critical biofilm growth throughout unmodified carbon felts allows continuous bioelectrochemical chain elongation from  $\text{CO}_2$  up to caproate at high current density. Under revision. 2017

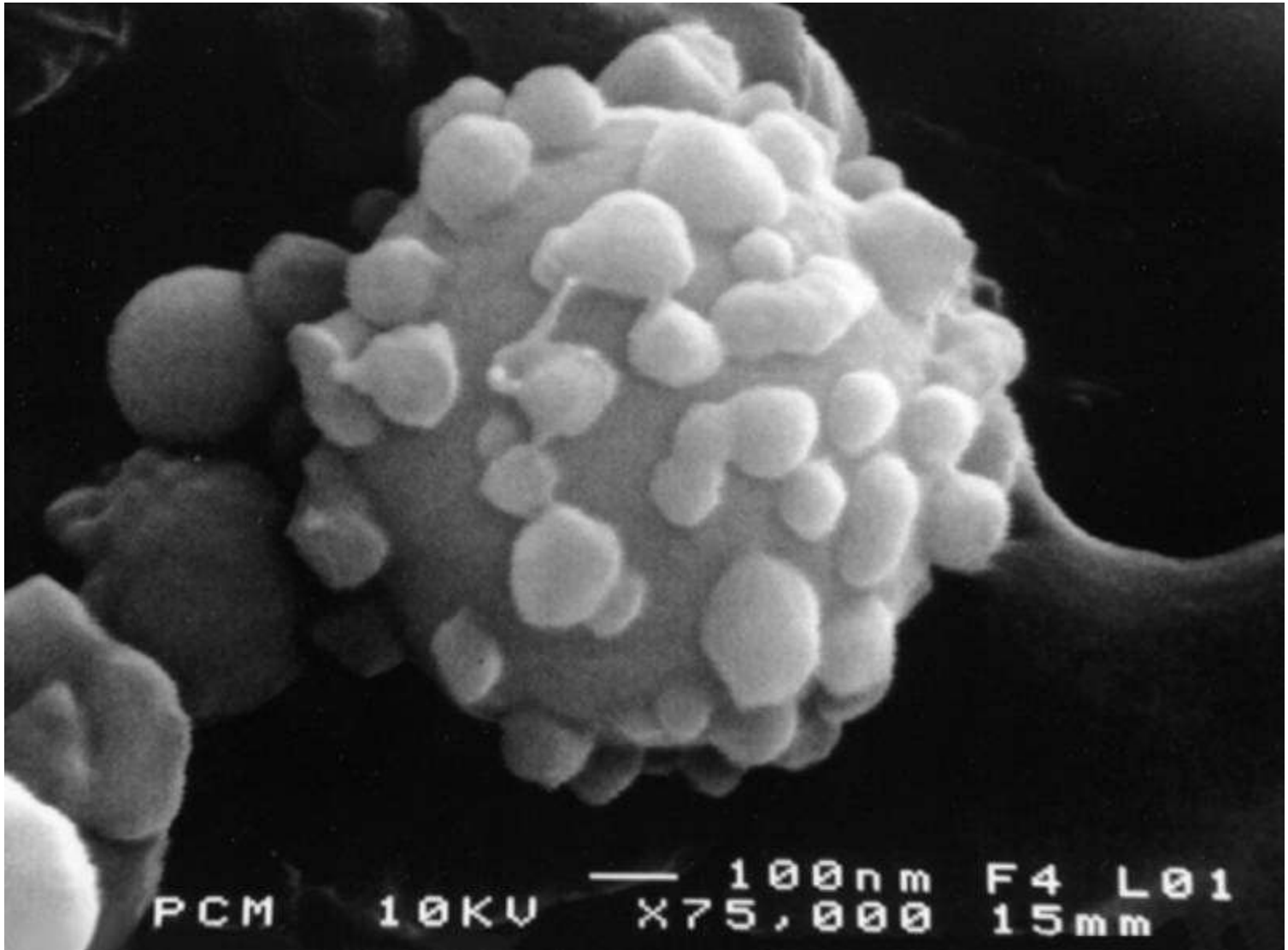
# Sulfur resources dependent on fossil fuels



# Biotechnological Sulfide Oxidation



# Sulfur Excreting Bacterium



# >200 H<sub>2</sub>S recovery systems

0.02 tpd S



0.5 tpd S



0.9 tpd S



2.8 tpd S



4 tpd S



13 tpd S





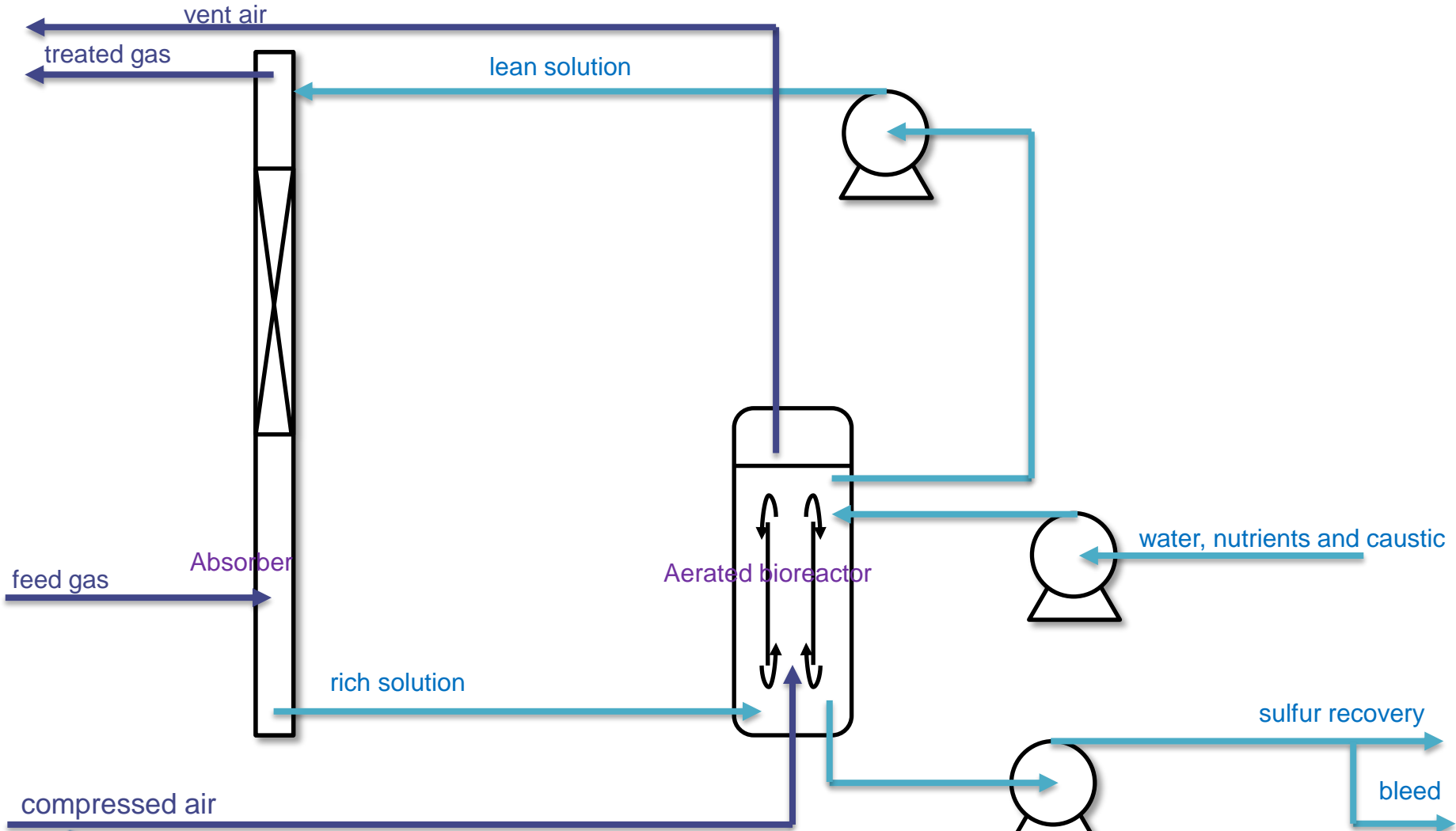
# Biosulfur as fertiliser

## University of Alberta (Canada)

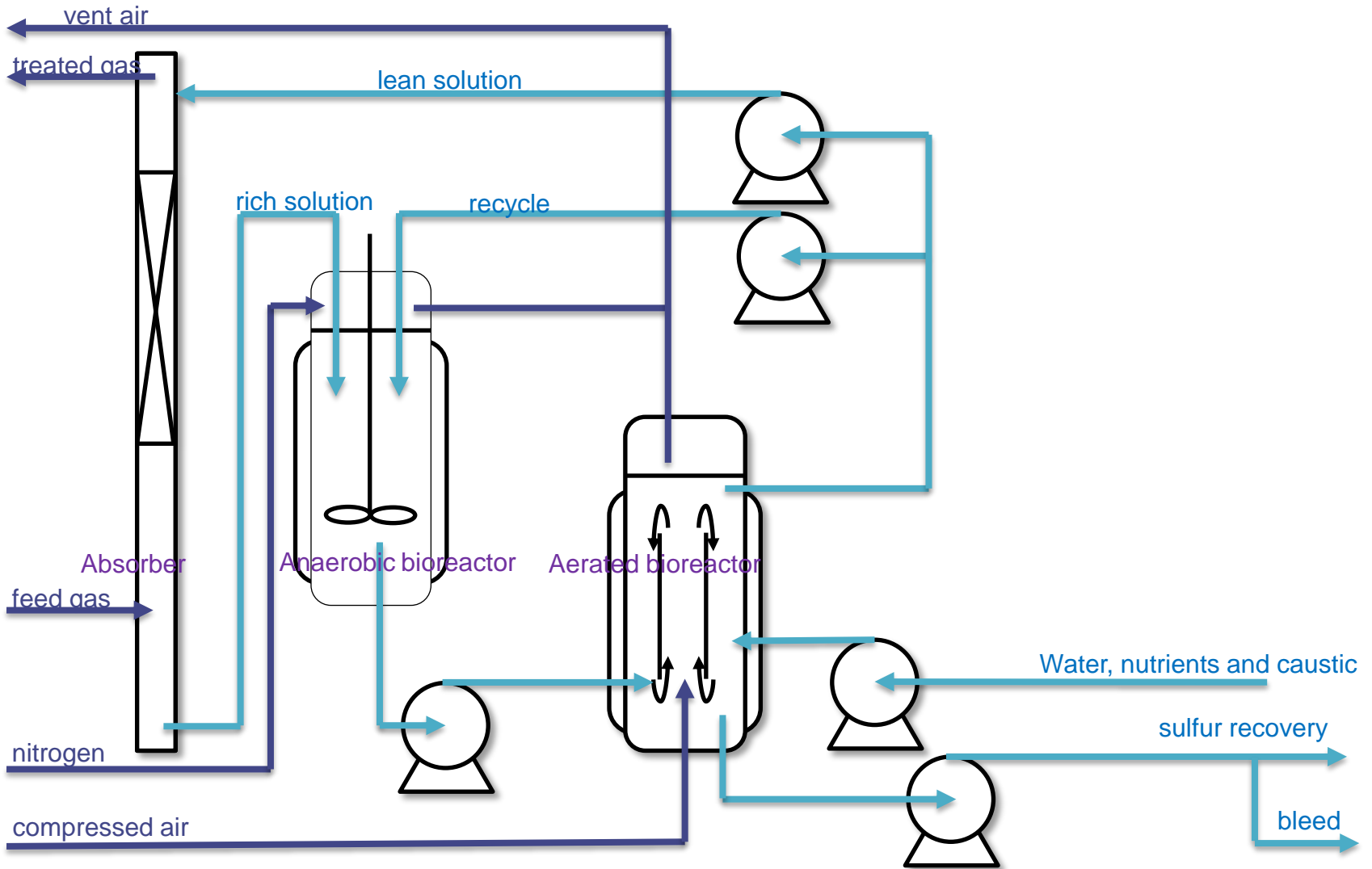
- Sulfur source      Canola yield (g/pot)  
   after 84 days
- 

- Reference test                      15.6
- S95                                      19.6
- T90CR                                16.1
- Agrium S                             20.2
- $(\text{NH}_4)_2\text{SO}_4$                       20.7
- **BIOSULFUR**                      **22.6**

# Conventional Thiopaq®



# New anaerobic step



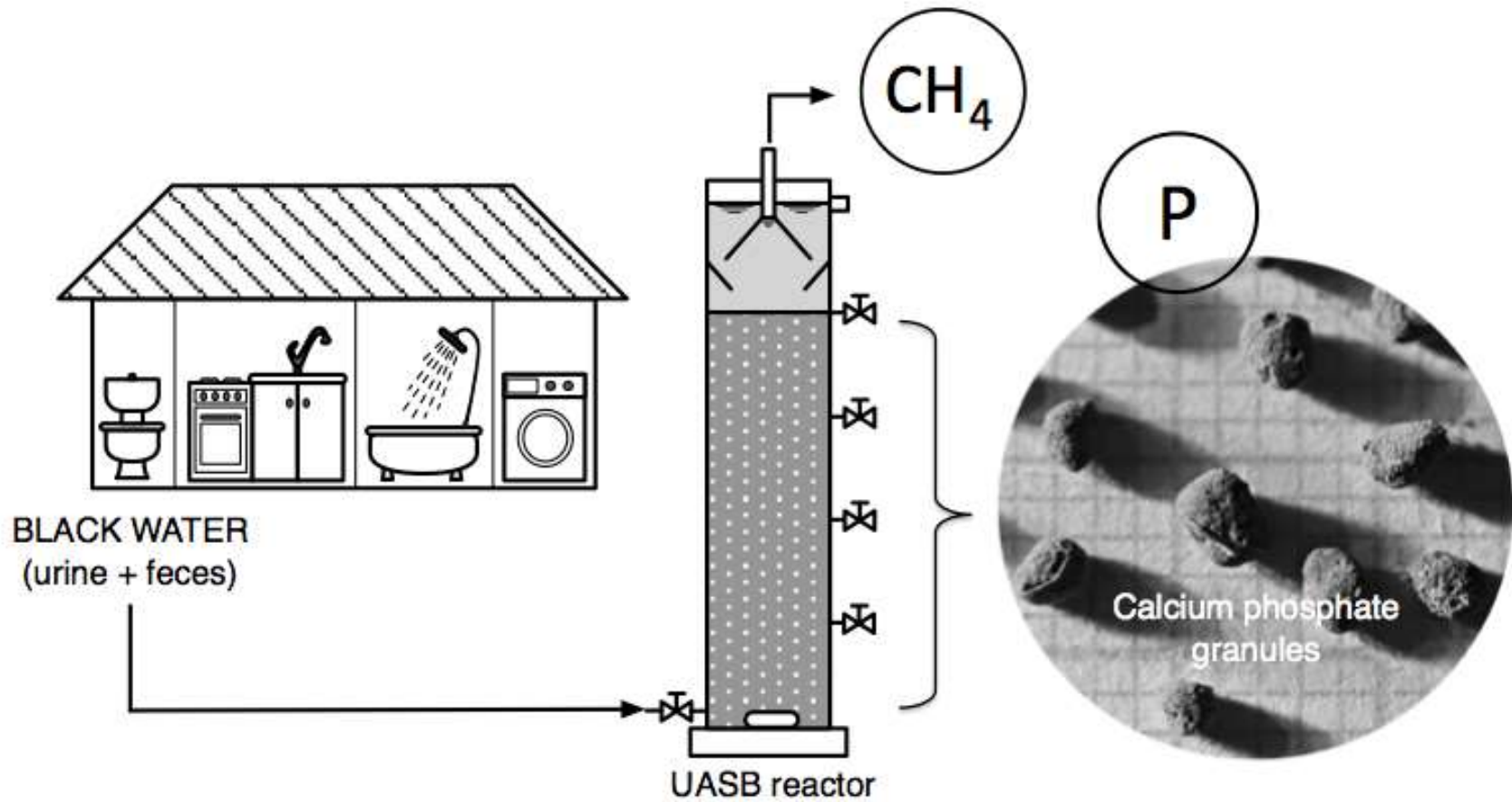
# Strong efficiency improvement

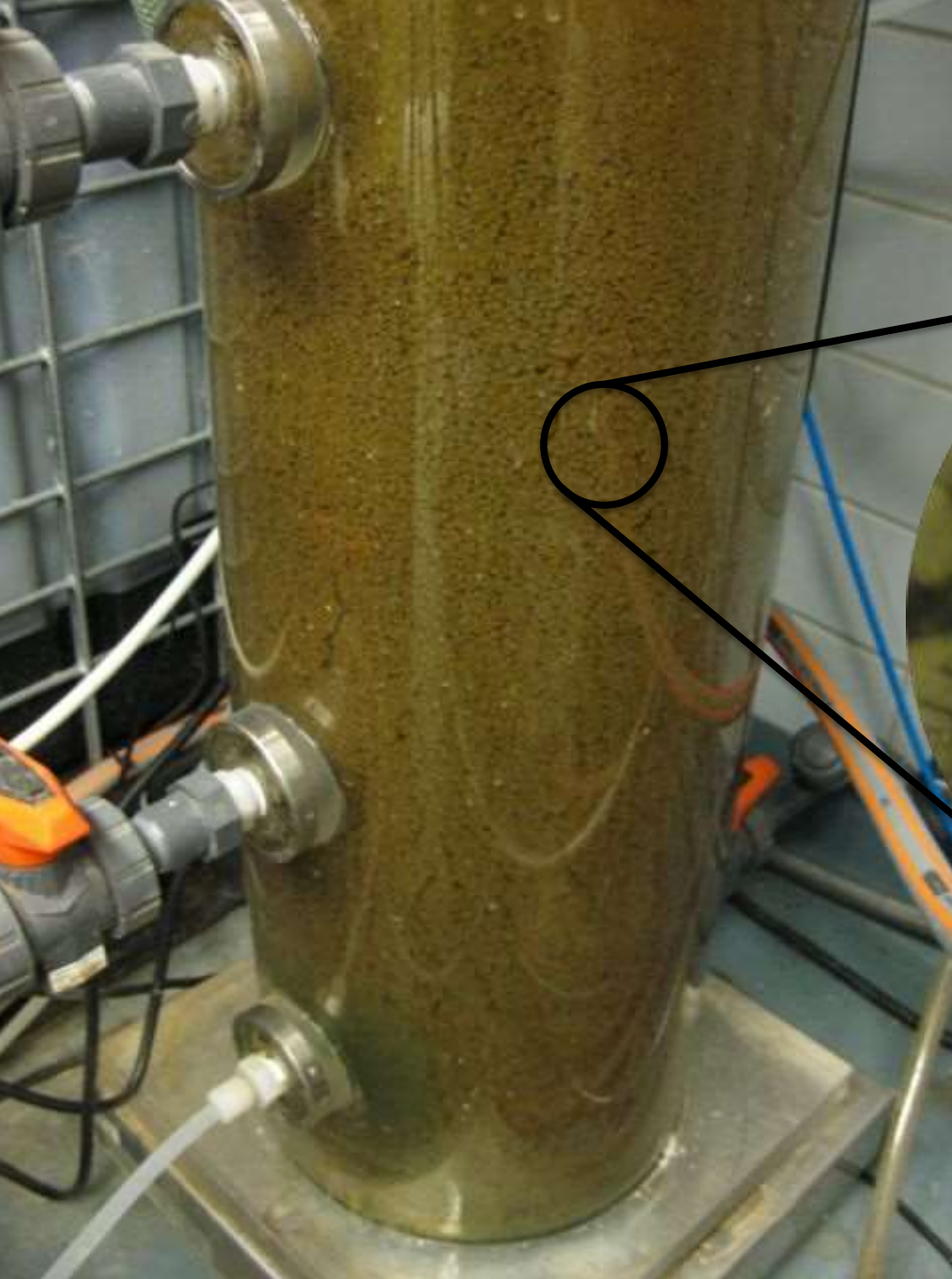
	<b>Traditional line-up (no anaerobic bioreactor)</b>	<b>New line-up (including anaerobic bioreactor)</b>
<b>S<sub>8</sub> (mol%)</b>	<b>90</b>	<b>97</b>
<b>SO<sub>4</sub><sup>2-</sup> (mol%)</b>	<b>5</b>	<b>2</b>
<b>S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (mol%)</b>	<b>5</b>	<b>1</b>
<b>Caustic use (kg NaOH/kgS)</b>	<b>0.35</b>	<b>0.1</b>

# Phosphate depletion

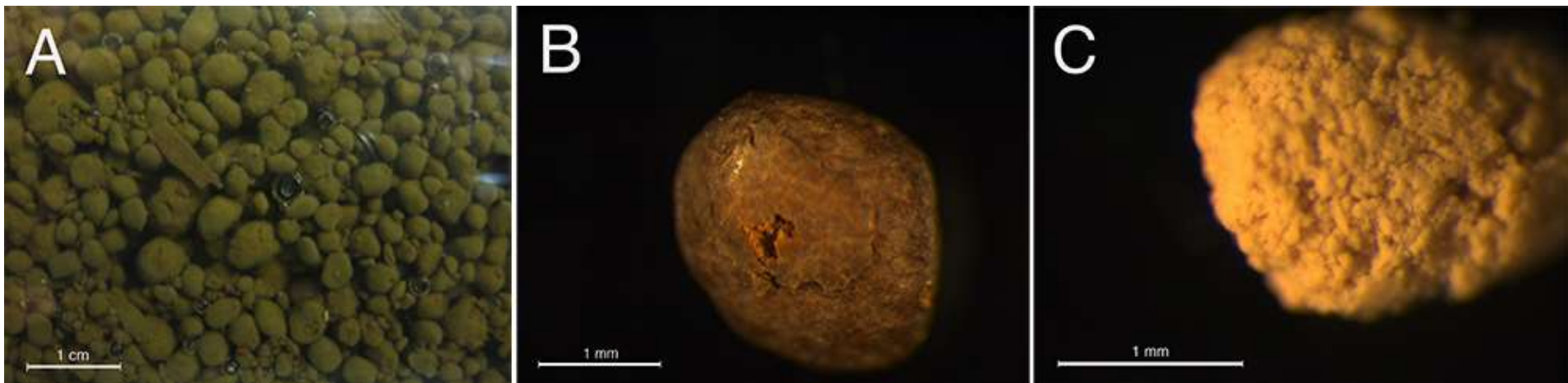


# Simultaneous recovery of CH<sub>4</sub> and P



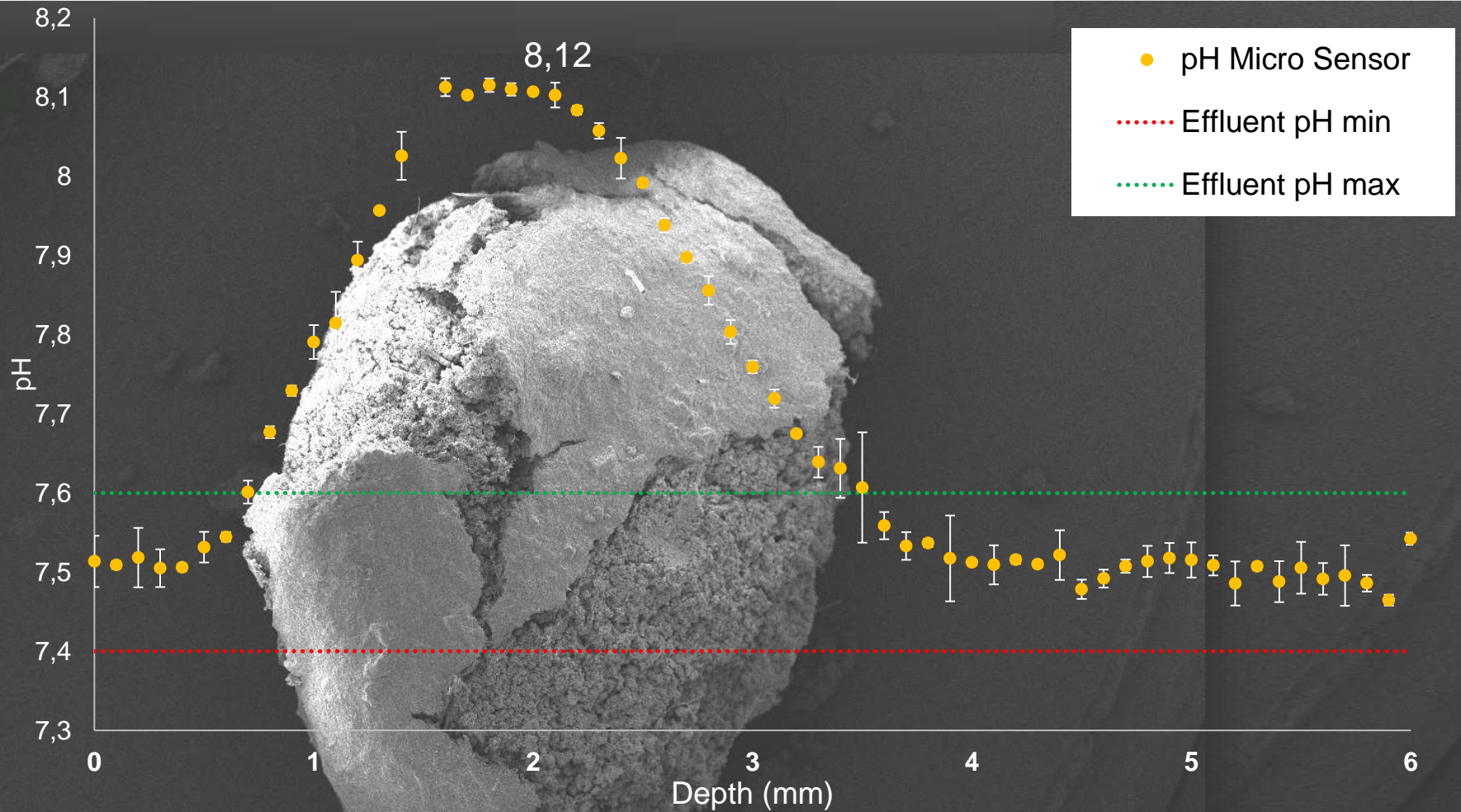


# Ca-P Crystals inside biofilm

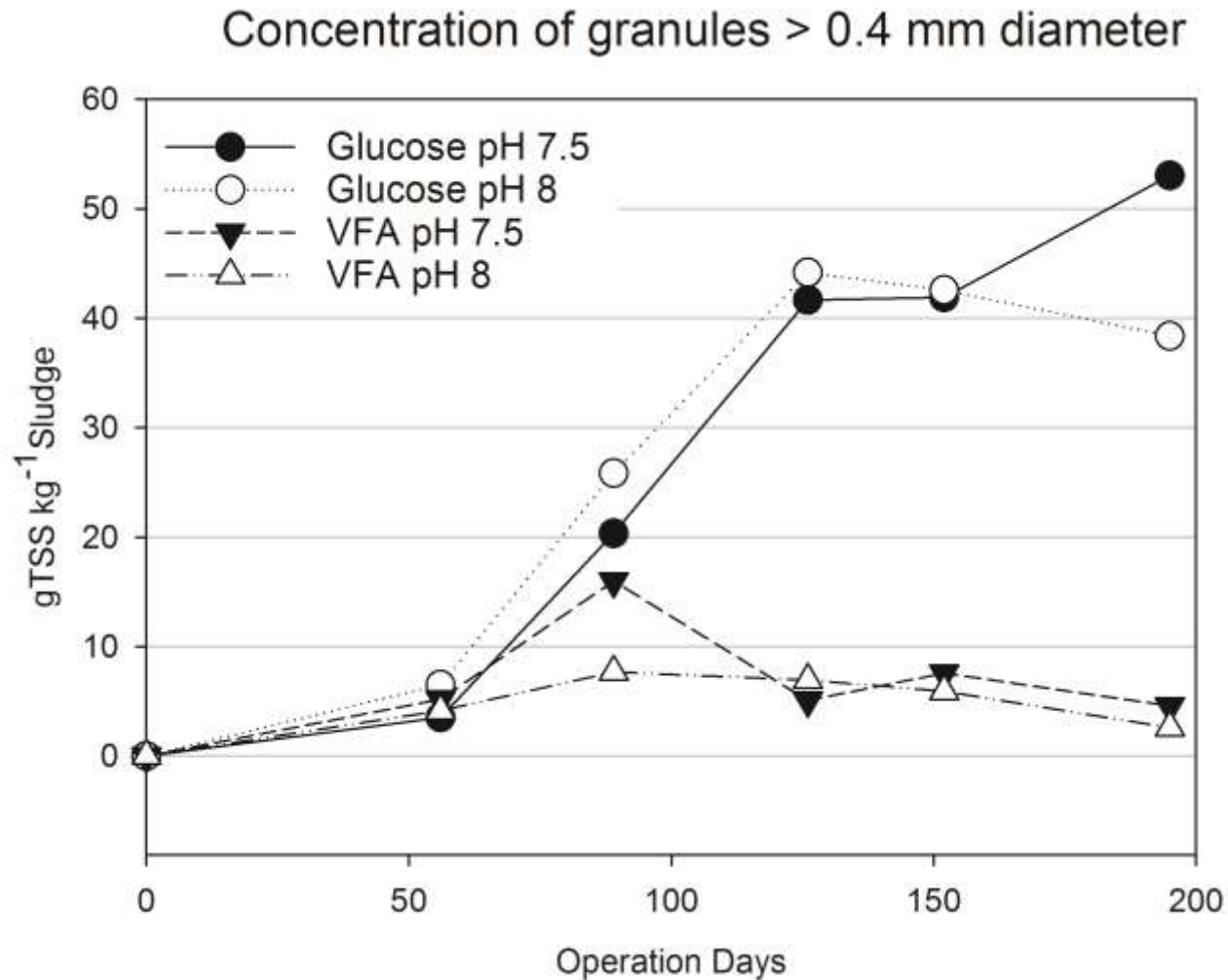




# pH profile across the granule



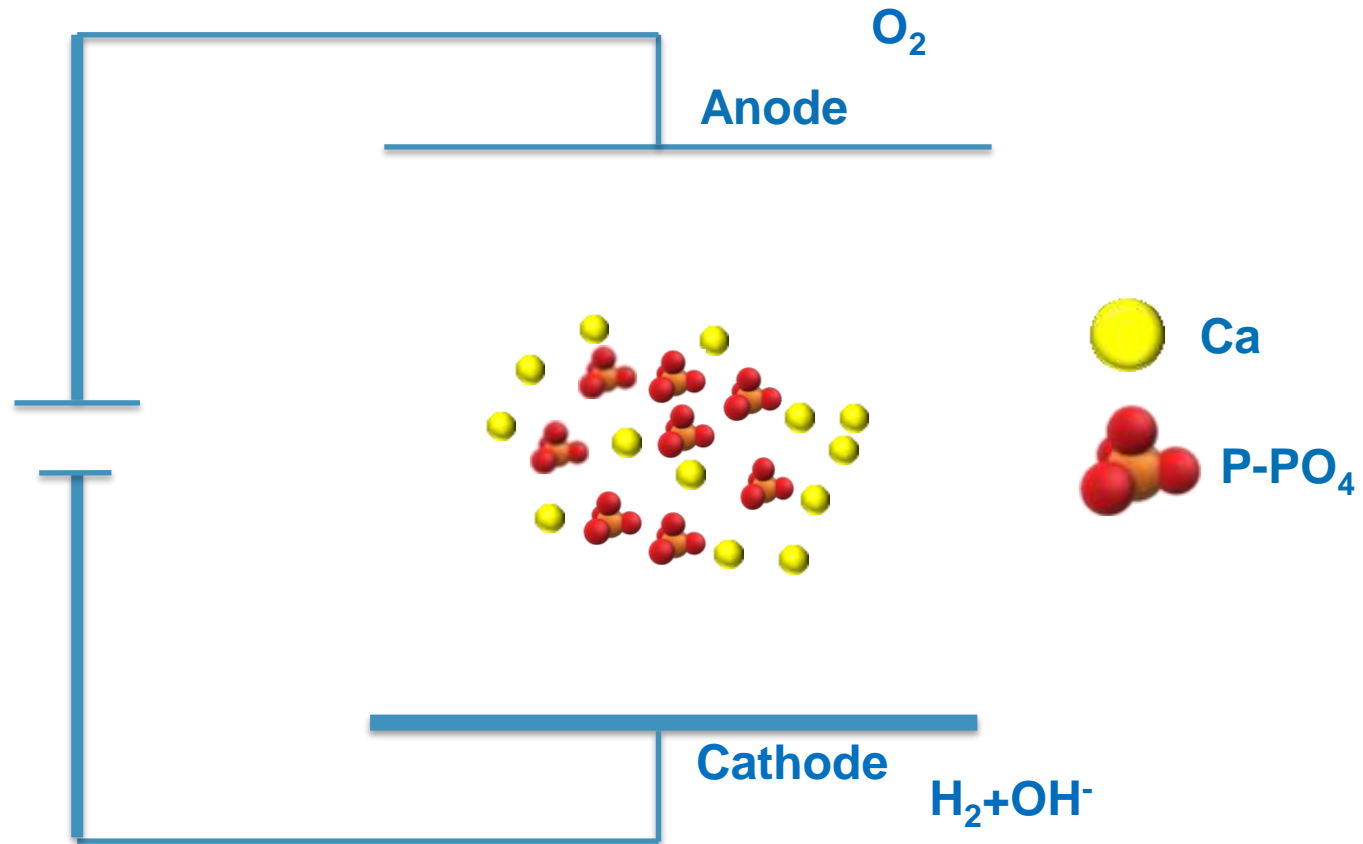
# Glucose enhances the formation and growth of $\text{Ca}_x(\text{PO}_4)_y$ granules



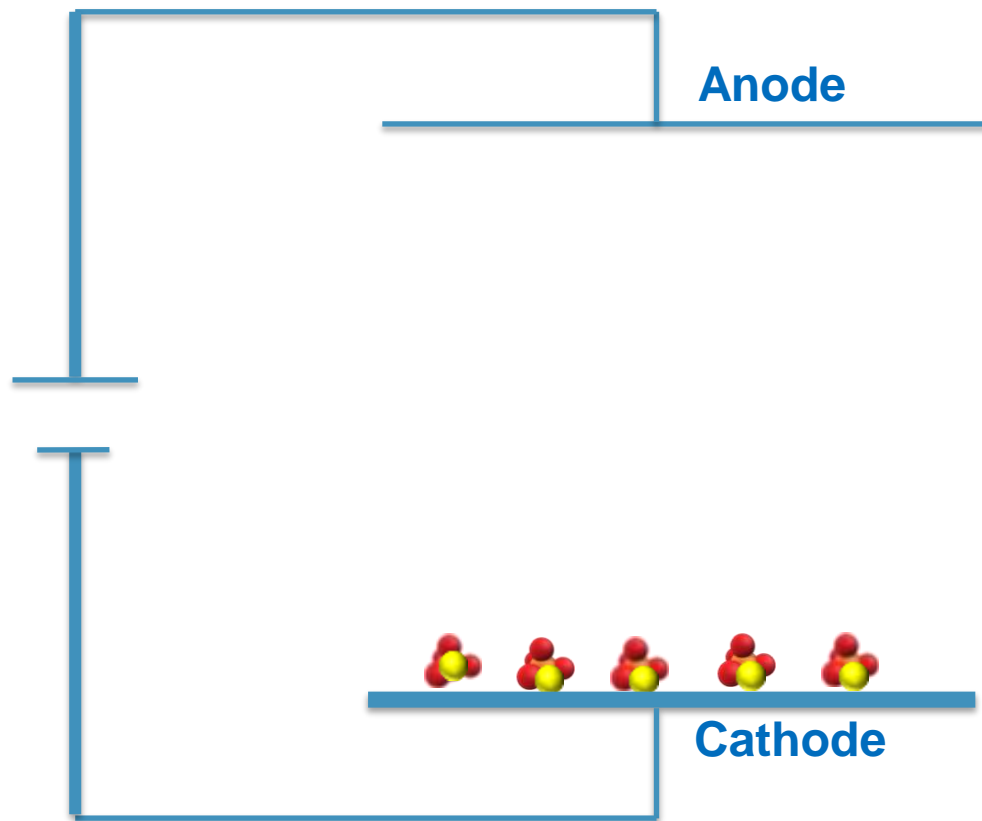
# Heavy metal content of P products (g/kg - P<sub>2</sub>O<sub>5</sub>)

Parameter	Unit	Bio-granules (demo-scale)	Phosphate rock
P <sub>2</sub> O <sub>5</sub>	%	41	40
Zn		743	1120
Cu		182	80
As		4	25
Cd	mg/kg	3	64
Cr	mg/kg	93	380

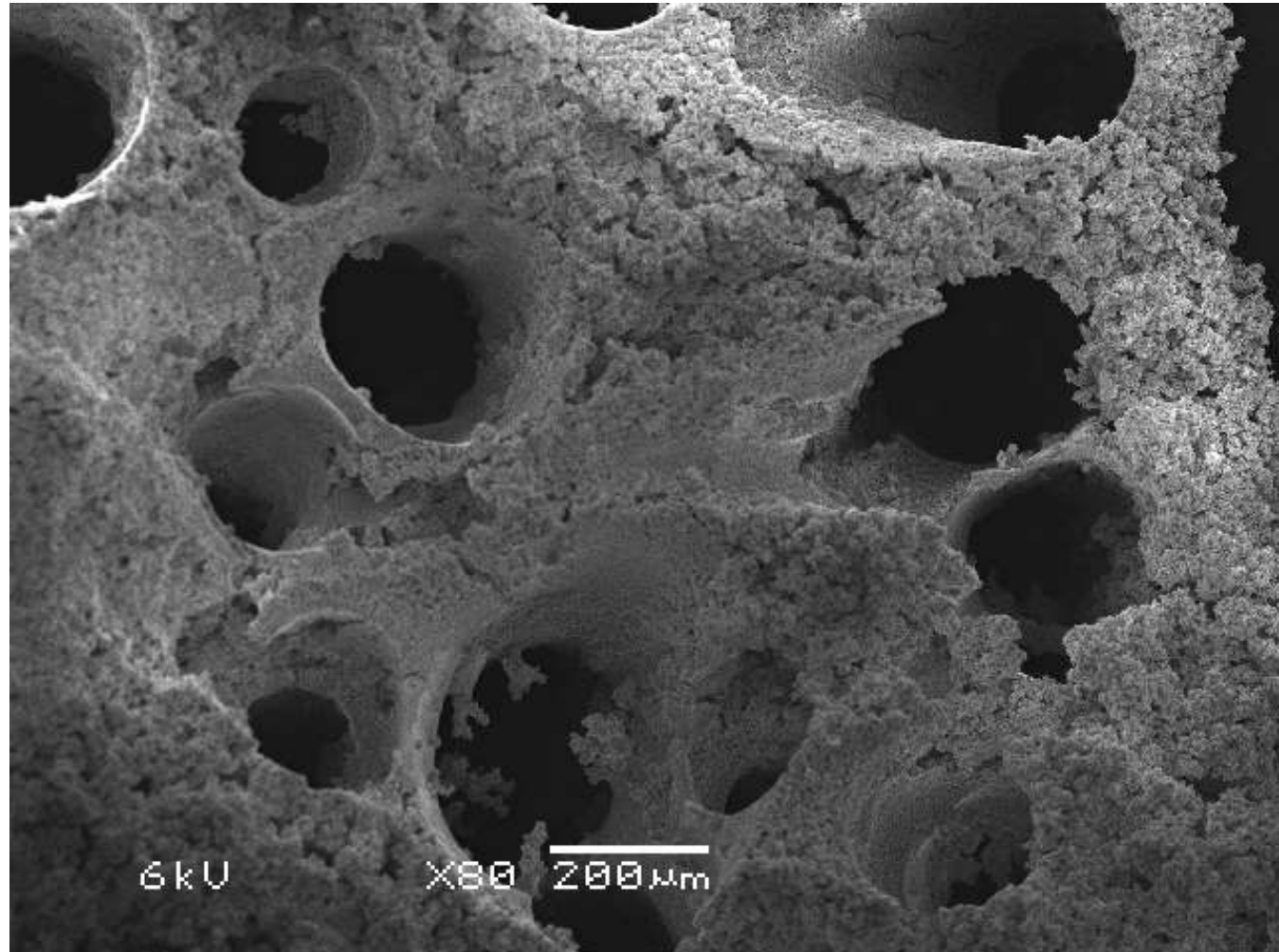
# Electrochemical phosphorus recovery



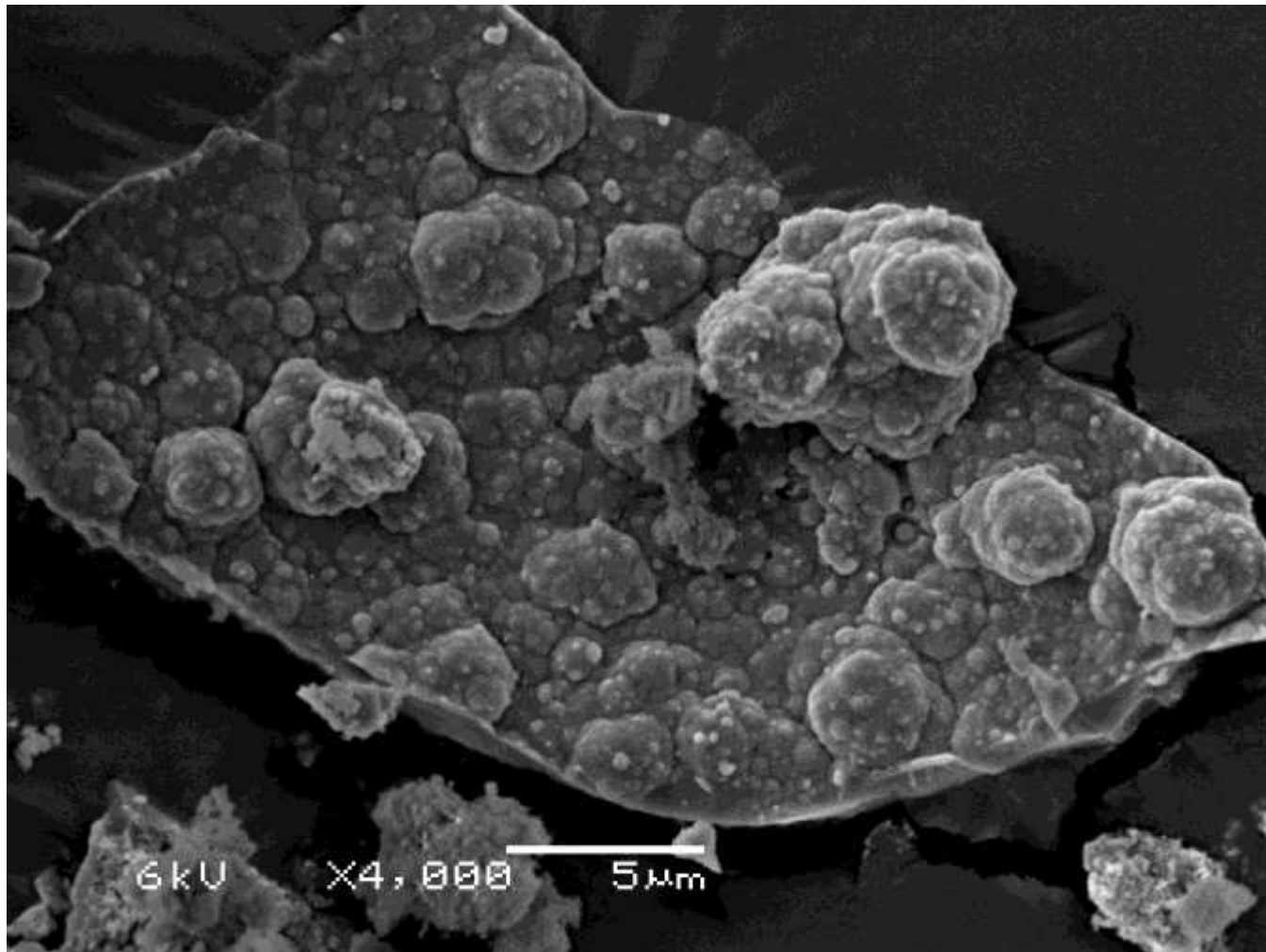
# Electrochemical phosphorus recovery



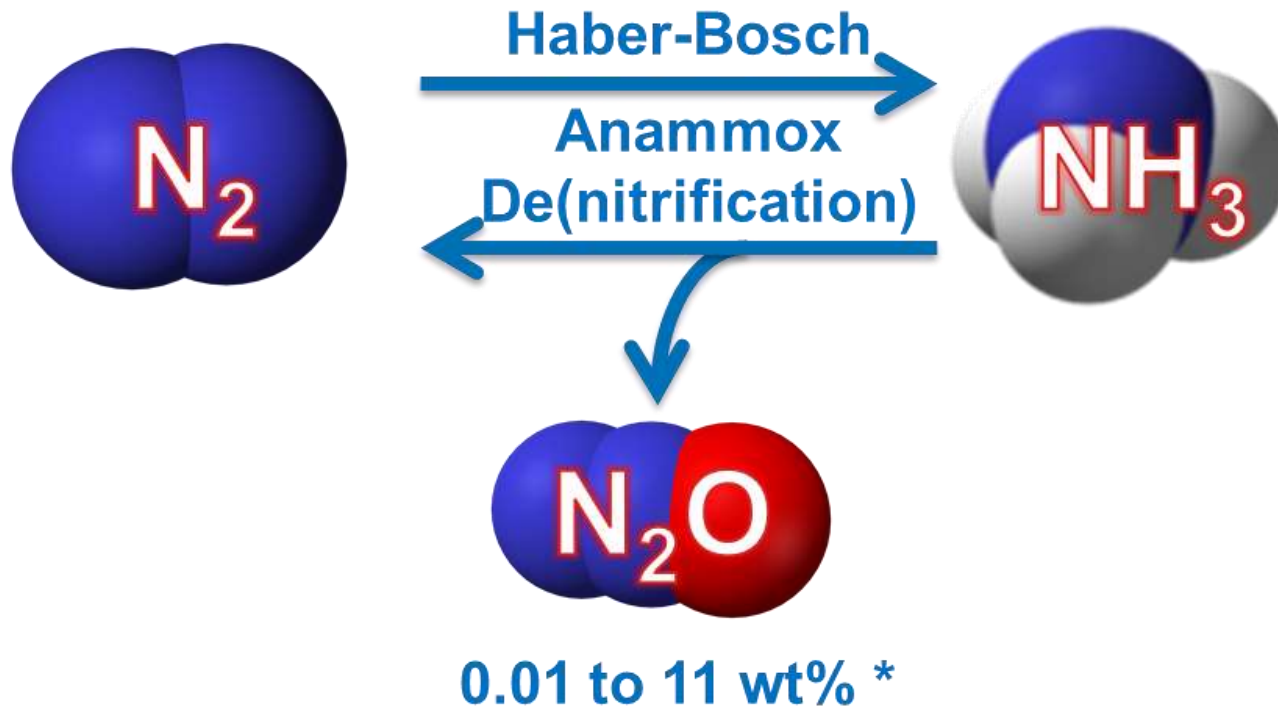
# SEM images of precipitates at the surface of cathode



# Amorphous calcium phosphate and calcium carbonate



# Nitrogen is an **climate issue**



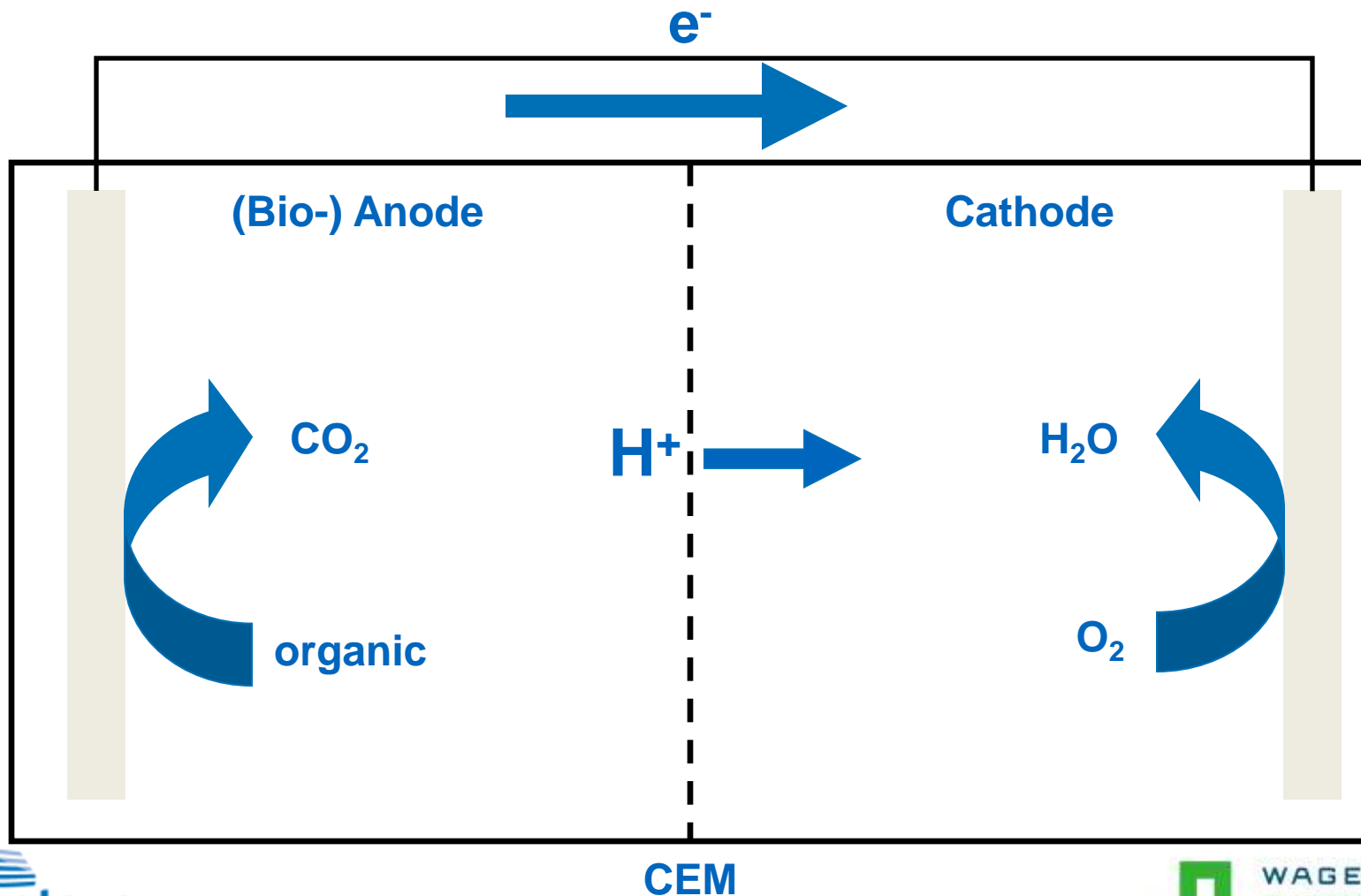


# Urine contains nitrogen in high concentration

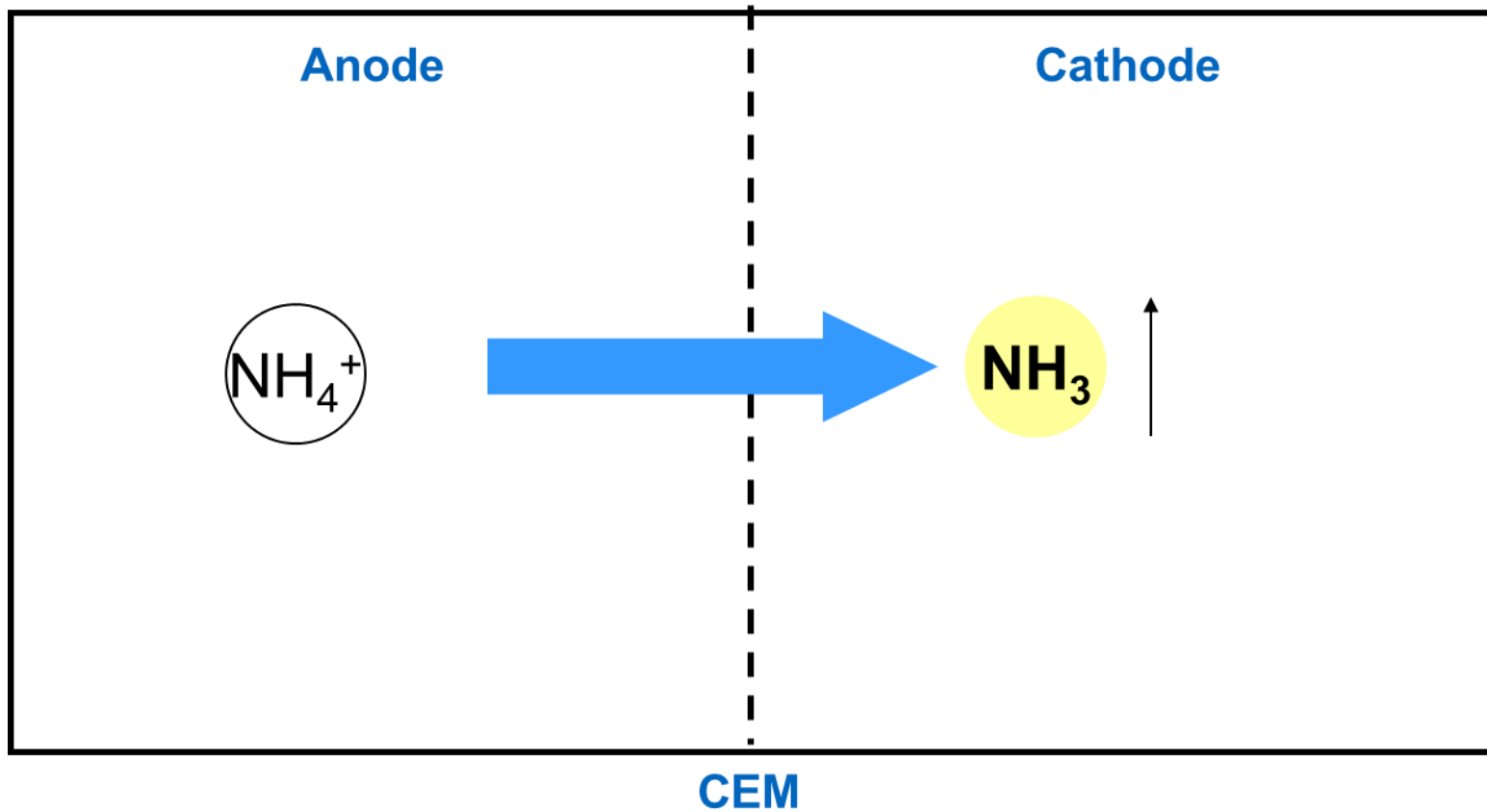
**Nitrogen**     9 g/L  
**COD**         10 g/L



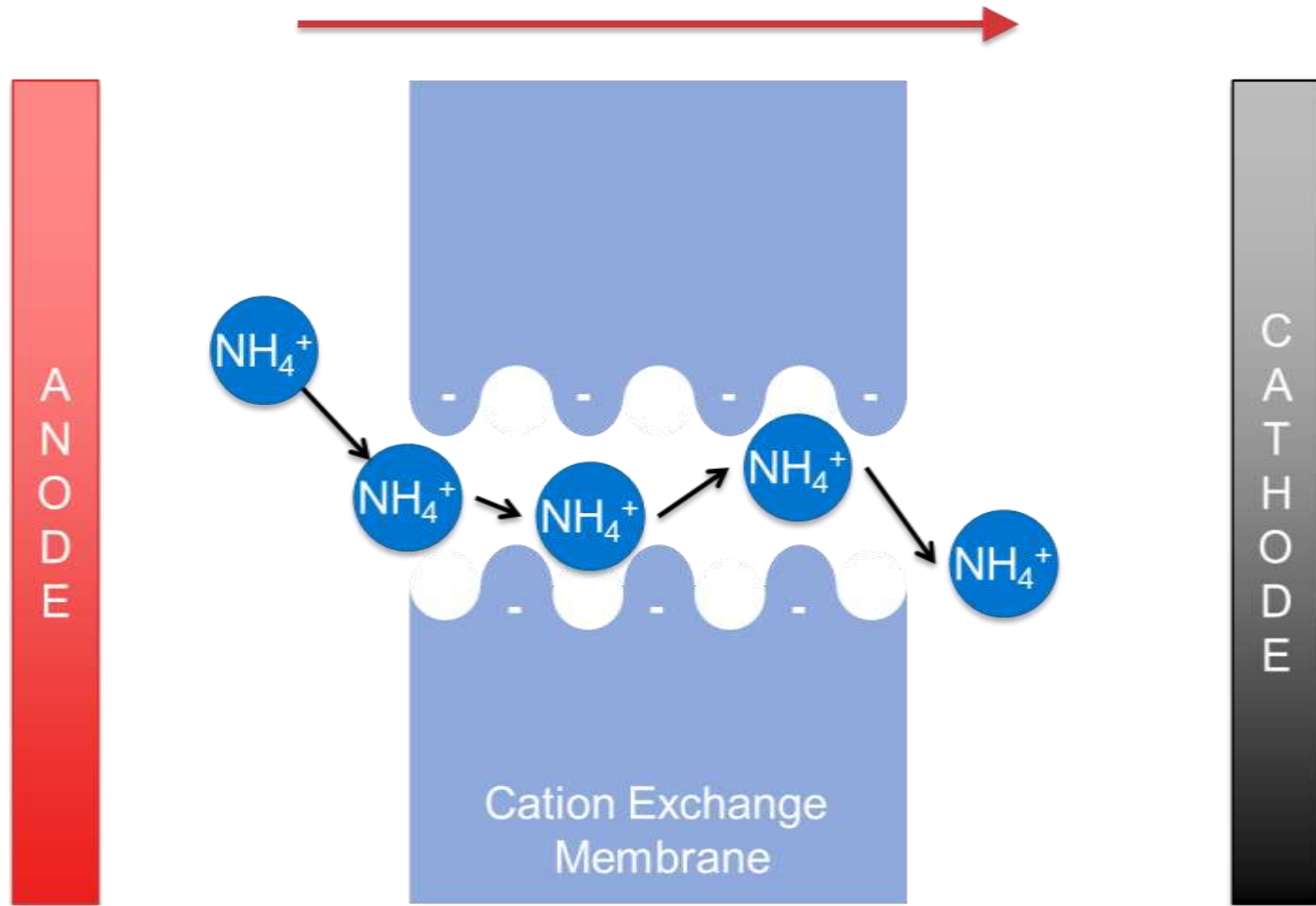
# Microbial Fuel Cell



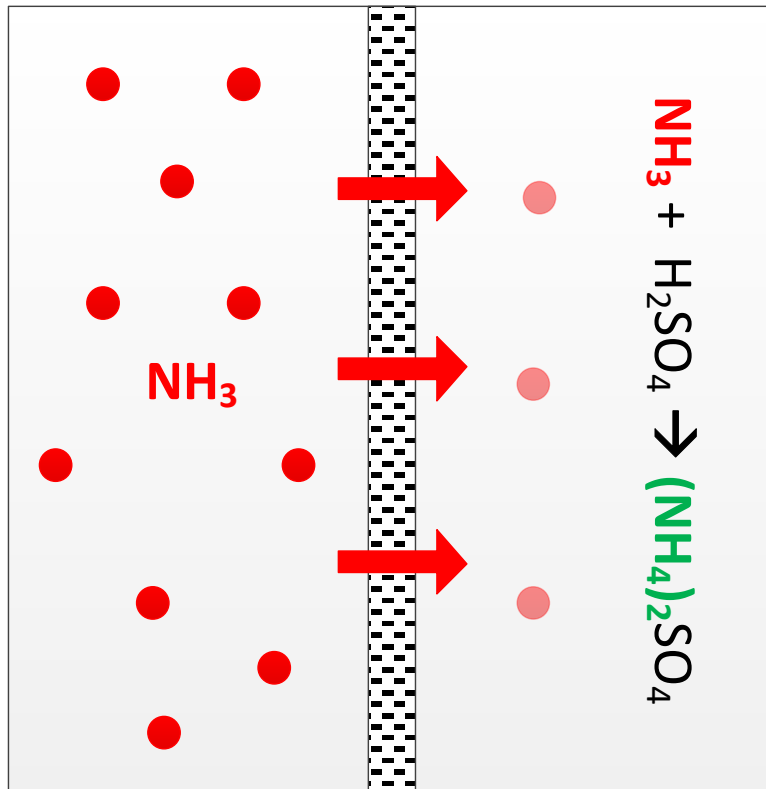
# Case Ammonia Recovery



# Current driven ammonia recovery



# TransMembraneChemiSorption

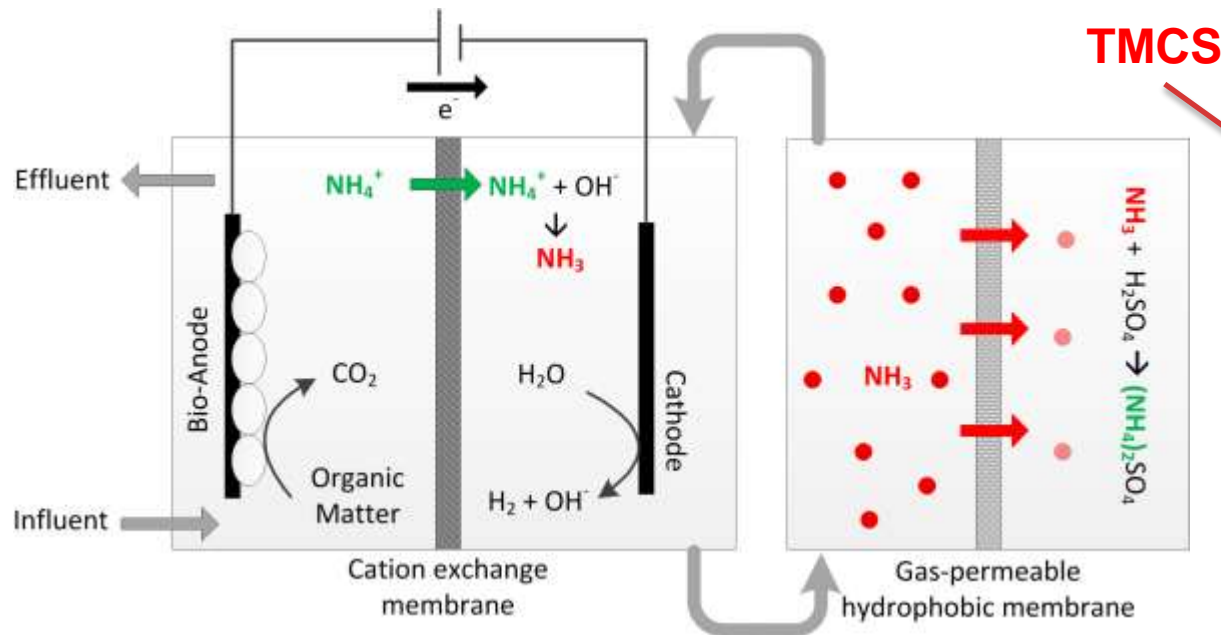


Gas-permeable  
hydrophobic membrane



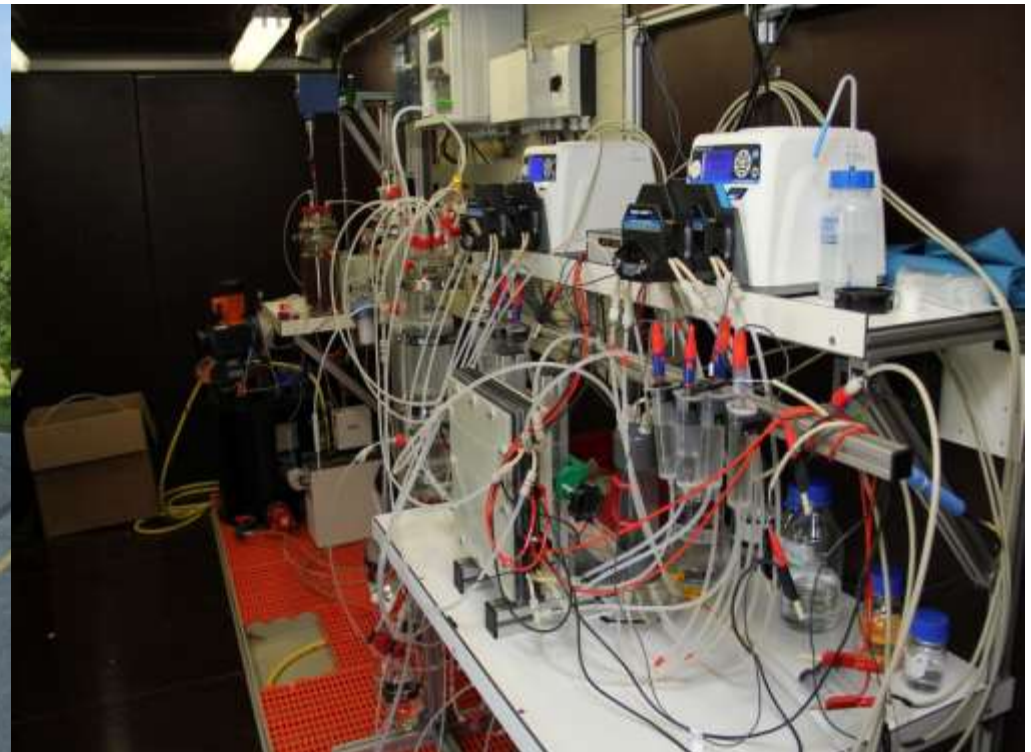
Commercial TMCS module  
size  $\sim 100\text{cm}^2$  (3cm x 3cm x 1cm)

# Trans membrane chemisorption (TMCS) integrated in the cathode of an BES



P. Kuntke, P. Zamora, M. Saakes, C. J. N. Buisman, H. V. M. Hamelers, Environmental Science: Water Research & Technology, (2016).

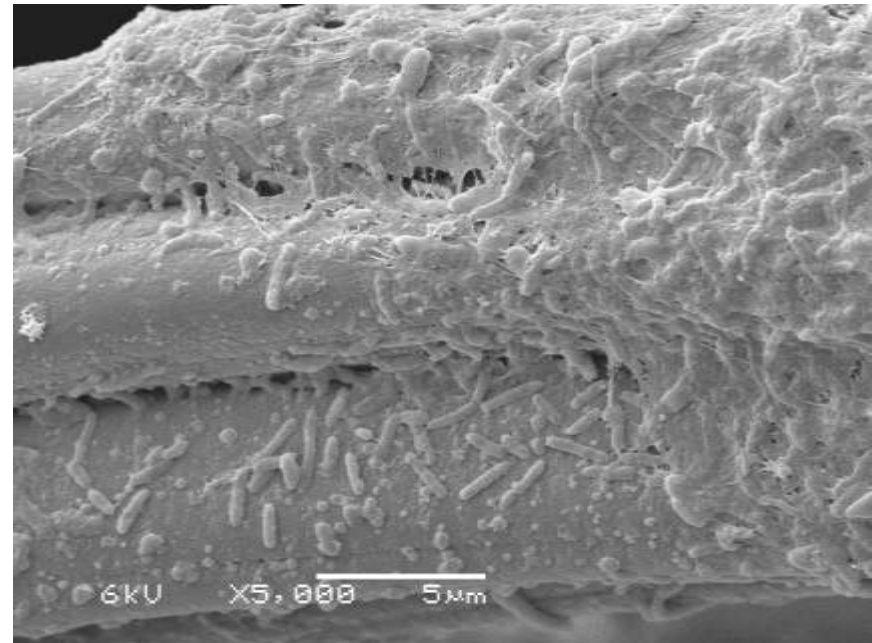
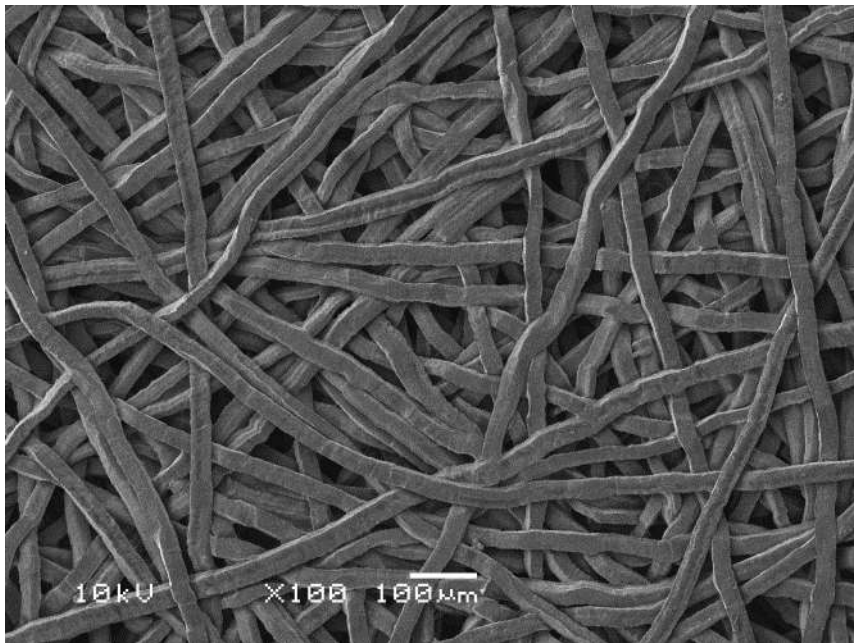
# Piloting urine MFC (30 persons)



# Current can be derived from (Bio-) Electrochemical System

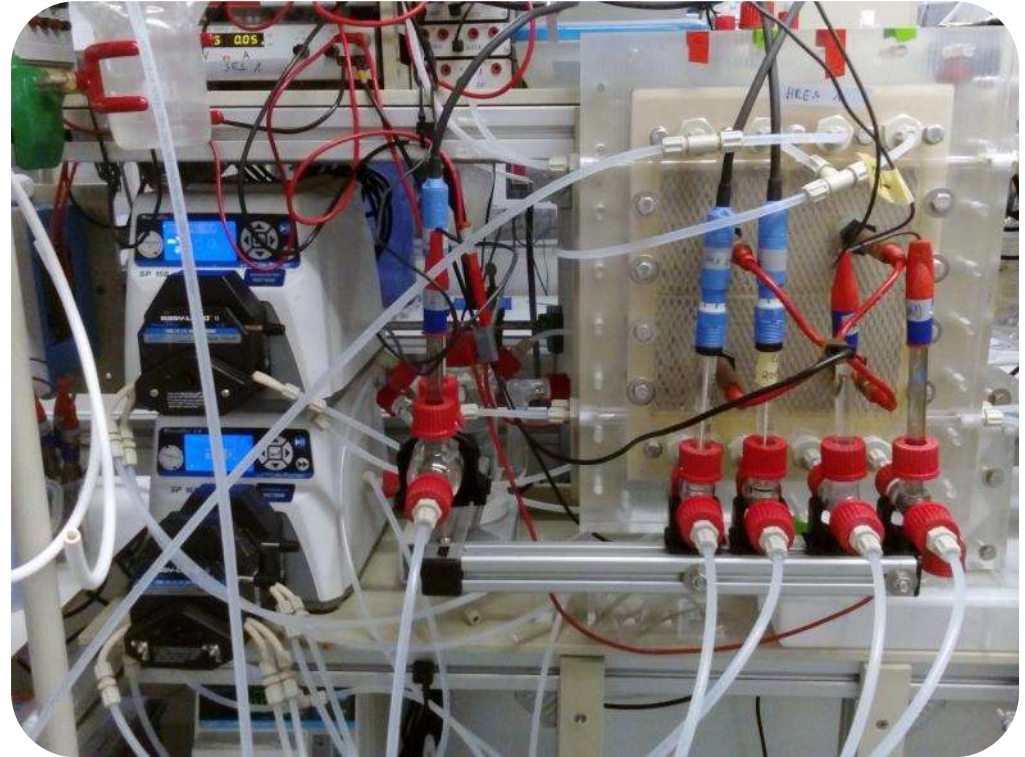
- ES
- High rates, but high energy input

- BES
- high rates, with low energy input





# Steps forward – up-scaling (4x)



# Hydrogen recycling allows for energy efficient ammonia recovery

Type of system		Energy demand MJ kg <sub>N</sub> <sup>-1</sup>
<b>HRES</b>		<b>6</b>
ES		12
Stripping		32
Anammox	+ HB	42 (5+37)
De(nitrification)	+ HB	51 (14+37)

Maurer et al., (2003) W.S.& T., 48, 1, 37-46  
Kuntke et al., to be submitted

# High transport rates in Electrochemical System allow for compact design

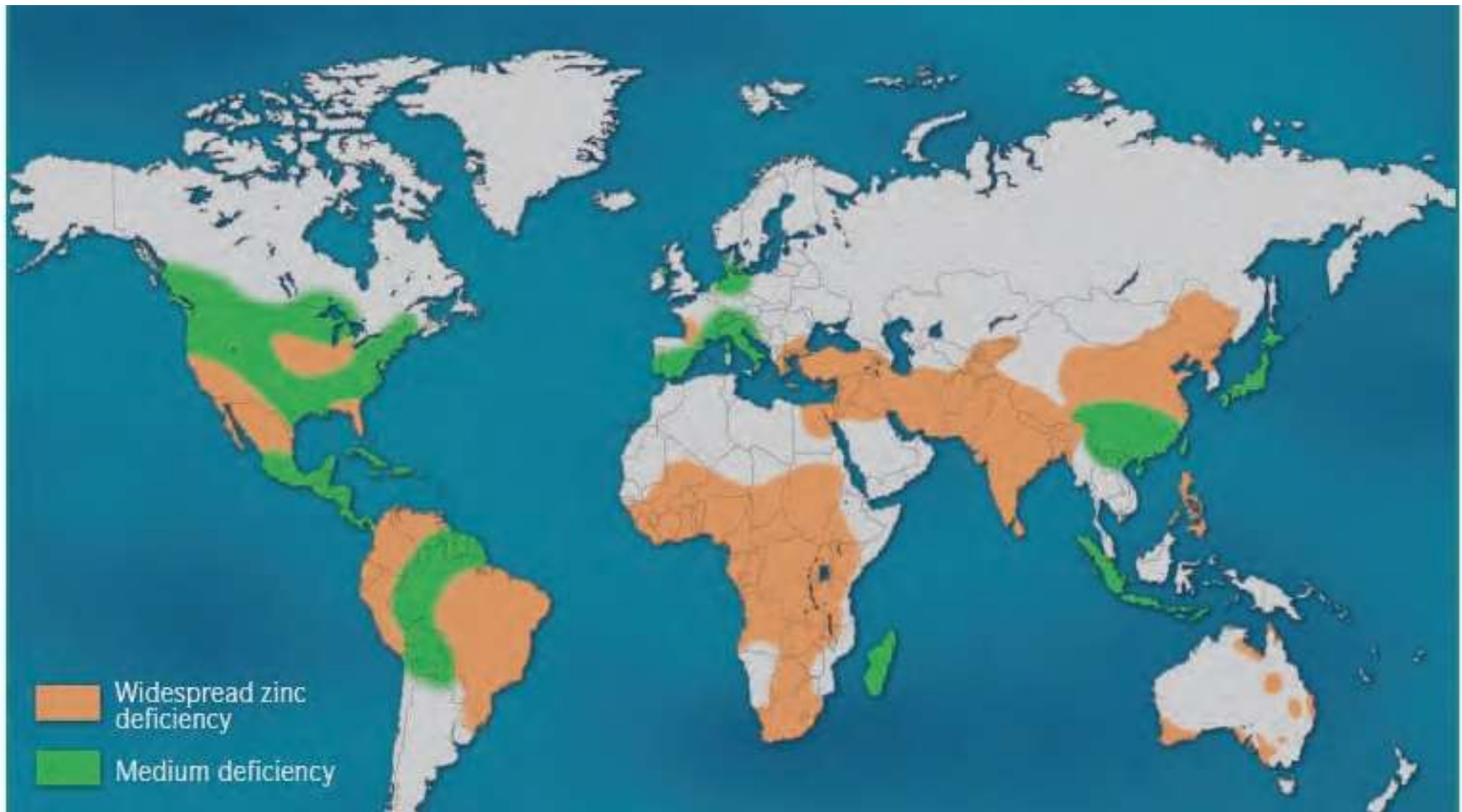
Type of system	Removal rate (kgN m <sup>-3</sup> d <sup>-1</sup> )
<b>HRES/ES</b>	<b>15</b>
Anammox	2
De(nitrification)	1

# Zinc deficiency effect



*Bron: Alloway 2008*

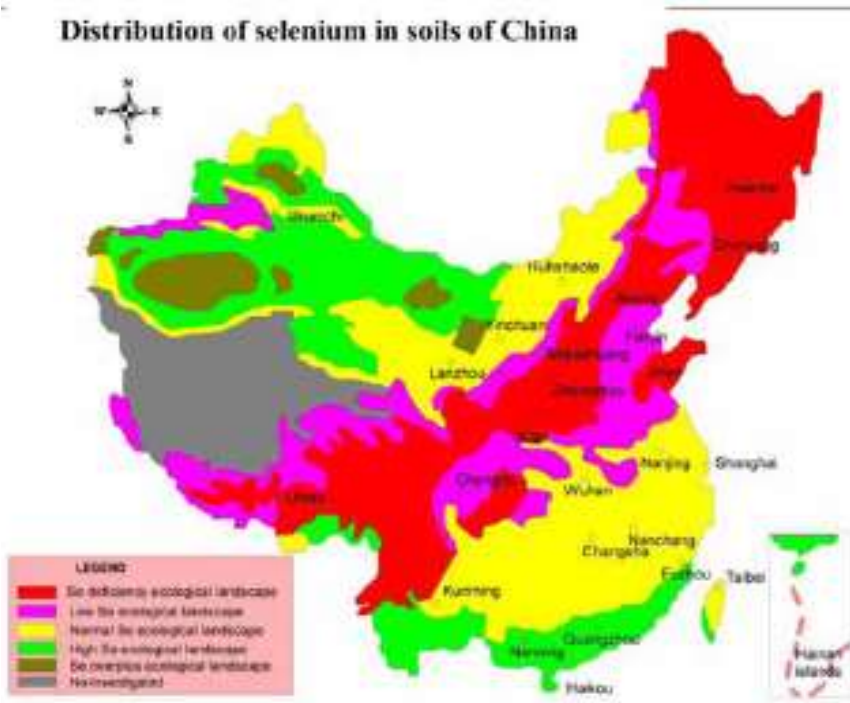
# World Zinc Deficiency



*Bron: Alloway 2008*

# Link between Se deficiency in soil and Se related disease in China

Distribution of selenium in soils of China

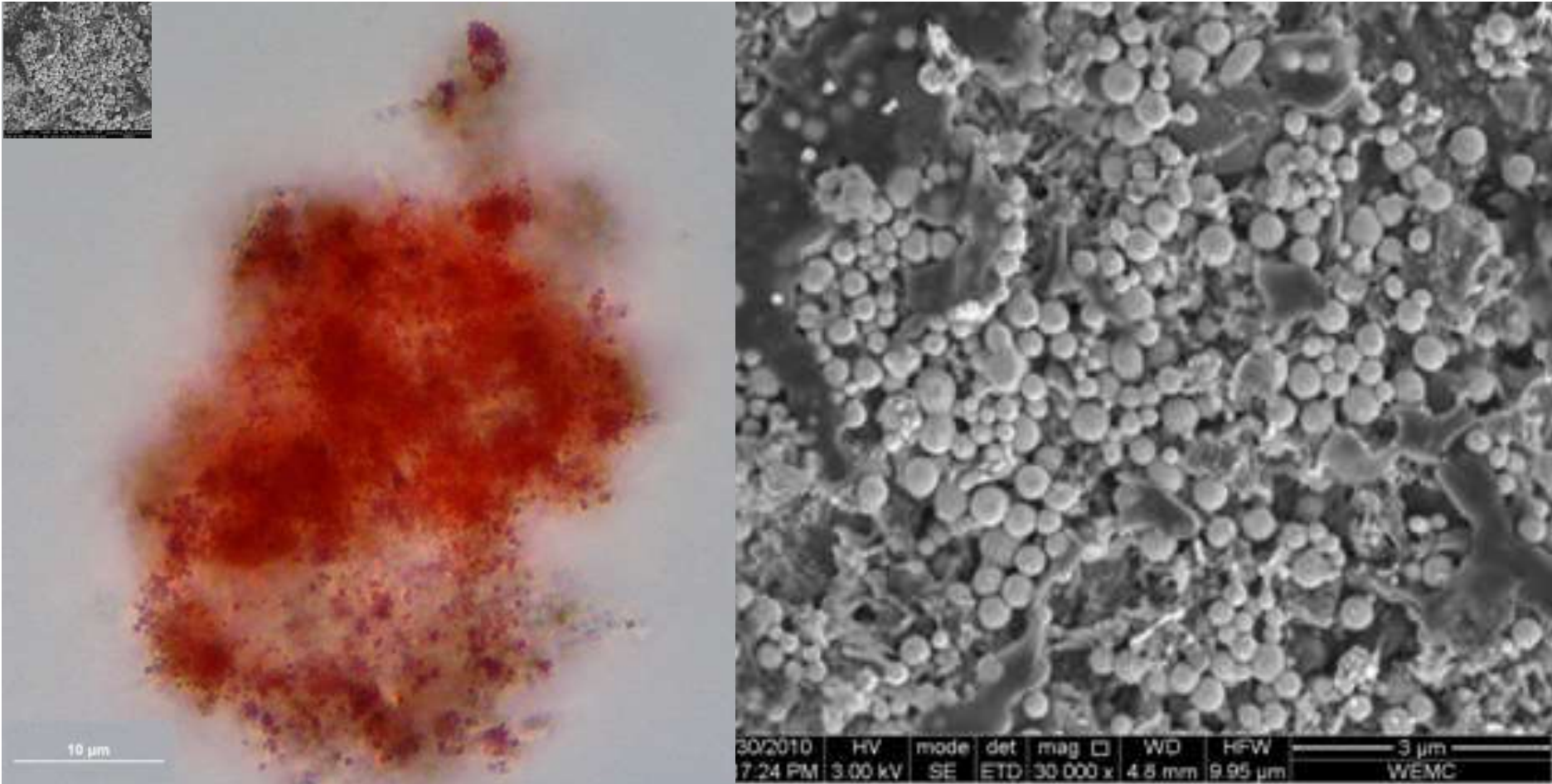


Bron: Alloway 2008

# Crystals by selenate reduction?

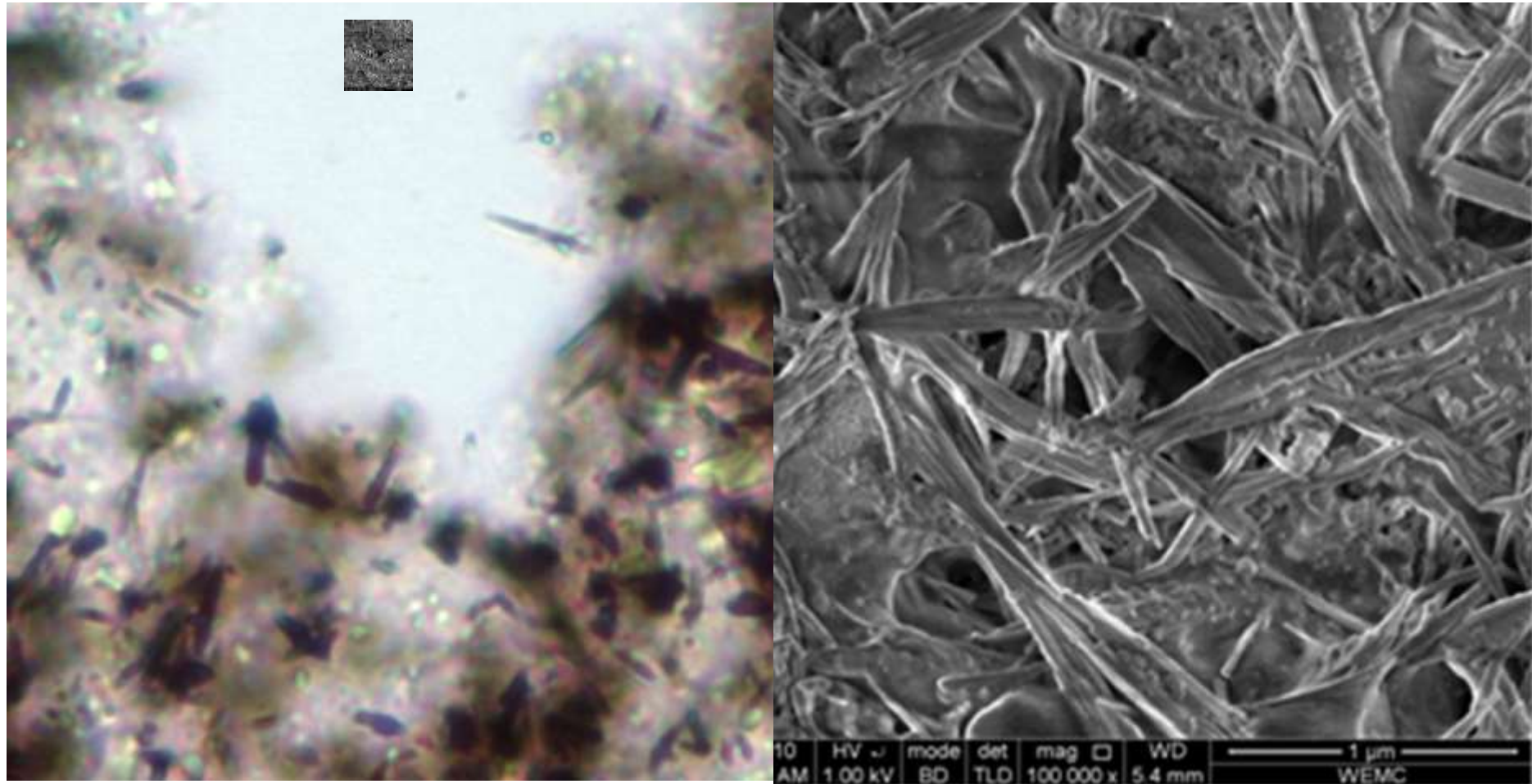


# Results T=30





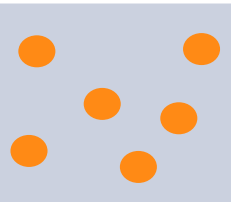
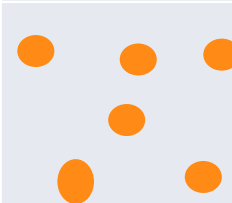
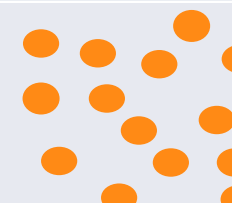
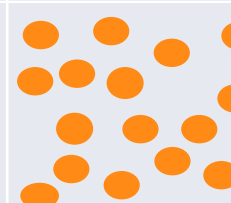
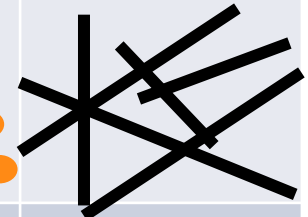
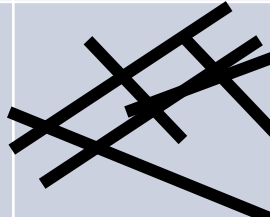
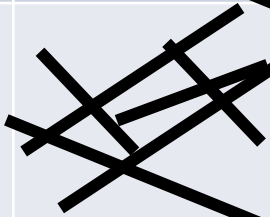
# Gray selenium 'needles' aciculair (50°)



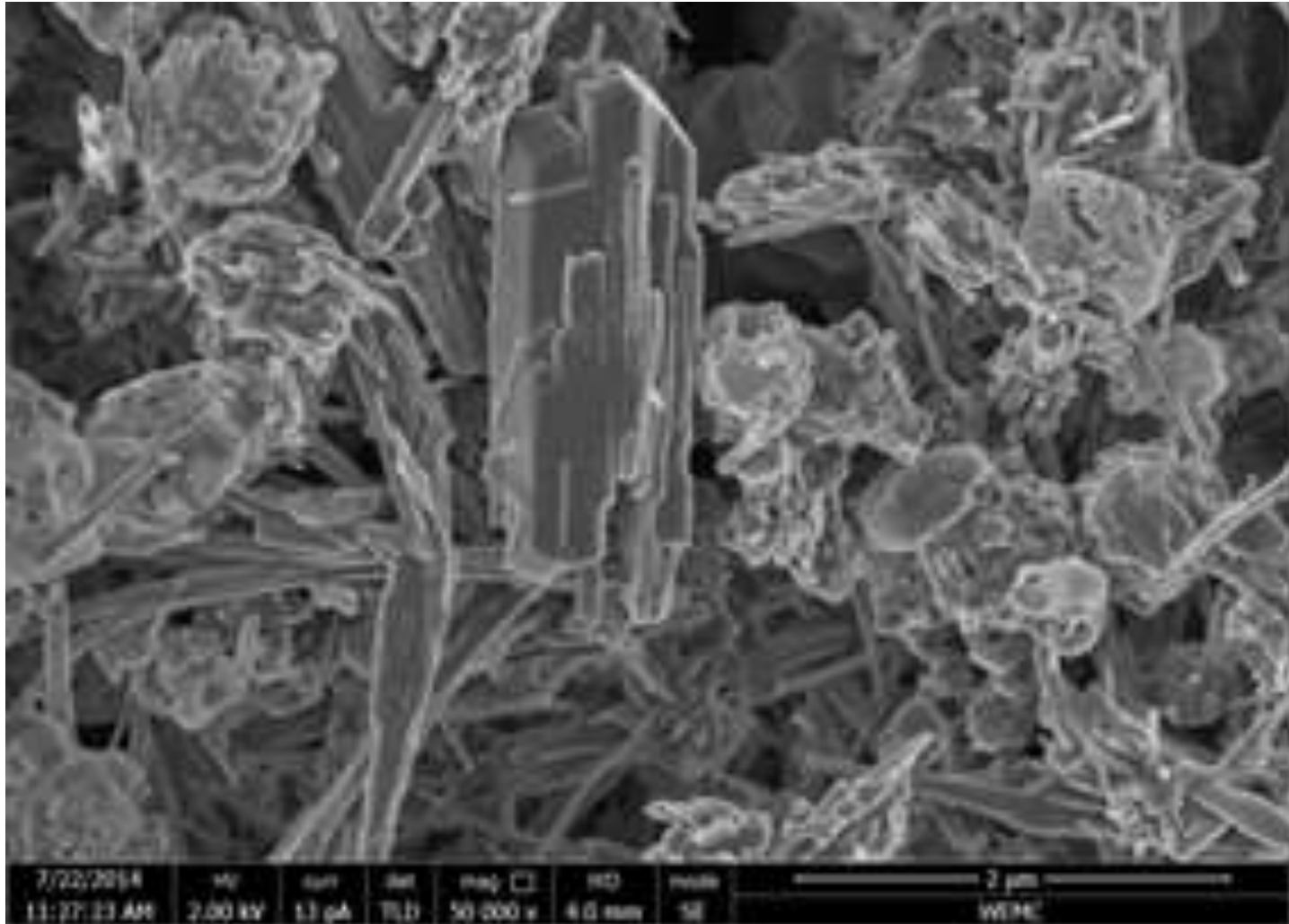
← 10 μm →

← 1 μm →

# Effect pH and Temperature

T(°C) pH(-)	20	30	40	50
6				
7				
8				
9				

# Crystalline selenium from reduced $\text{SeS}_2$



# Increase in selenium particles ( $\mu\text{m}^3$ )

<b>amorf sferical</b>	<b>0.07</b>
<b>crystalline aciculair</b>	<b>2</b>
<b>crystalline particles (via <math>\text{SeS}_2</math>)</b>	<b>700</b>

# Environmental Technology

## Biorecovery

Our research focuses on *bio-based technologies for recovery of valuable components from residual streams in the form of fuels, electricity, sulphur, copper, and phosphate.*



## Urban System Engineering

Scale and speed of urbanization leads to new challenges for our urban services. Closed resource cycles are necessary. We focus on *new sustainable biorecovery and cleaning concepts for management of urban and industrial water, sanitation, waste, nutrient and energy. Feedbacks from cities to agriculture are also studied.*



## Reusable Water

Water shortage threatens billions of people. Reuse and protection of our water sources are essential. Our research focuses on *removal of nutrients, pathogens nutrients, pathogens from water.*





Bio recovery group 2016

## For more information:

[www.wetsus.eu](http://www.wetsus.eu) & [www.ete.wur.nl](http://www.ete.wur.nl)  
[www.watercampus.nl](http://www.watercampus.nl)  
[www.topsectorwater.nl](http://www.topsectorwater.nl)

### Wetsus is co-funded by

- the Dutch Ministry of Economic Affairs (TKI-Topsector Water)
- the Dutch Ministry of Infrastructure and the Environment
- the European Union (Horizon 2020 and Seventh Framework Programme)
- Northern Netherlands Provinces (REP-SNN)
- the City of Leeuwarden, the Province of Fryslân
- The Netherlands Organisation for Scientific Research (from 2017 onwards)



Ministry of Economic Affairs



Ministry of Infrastructure and the Environment

