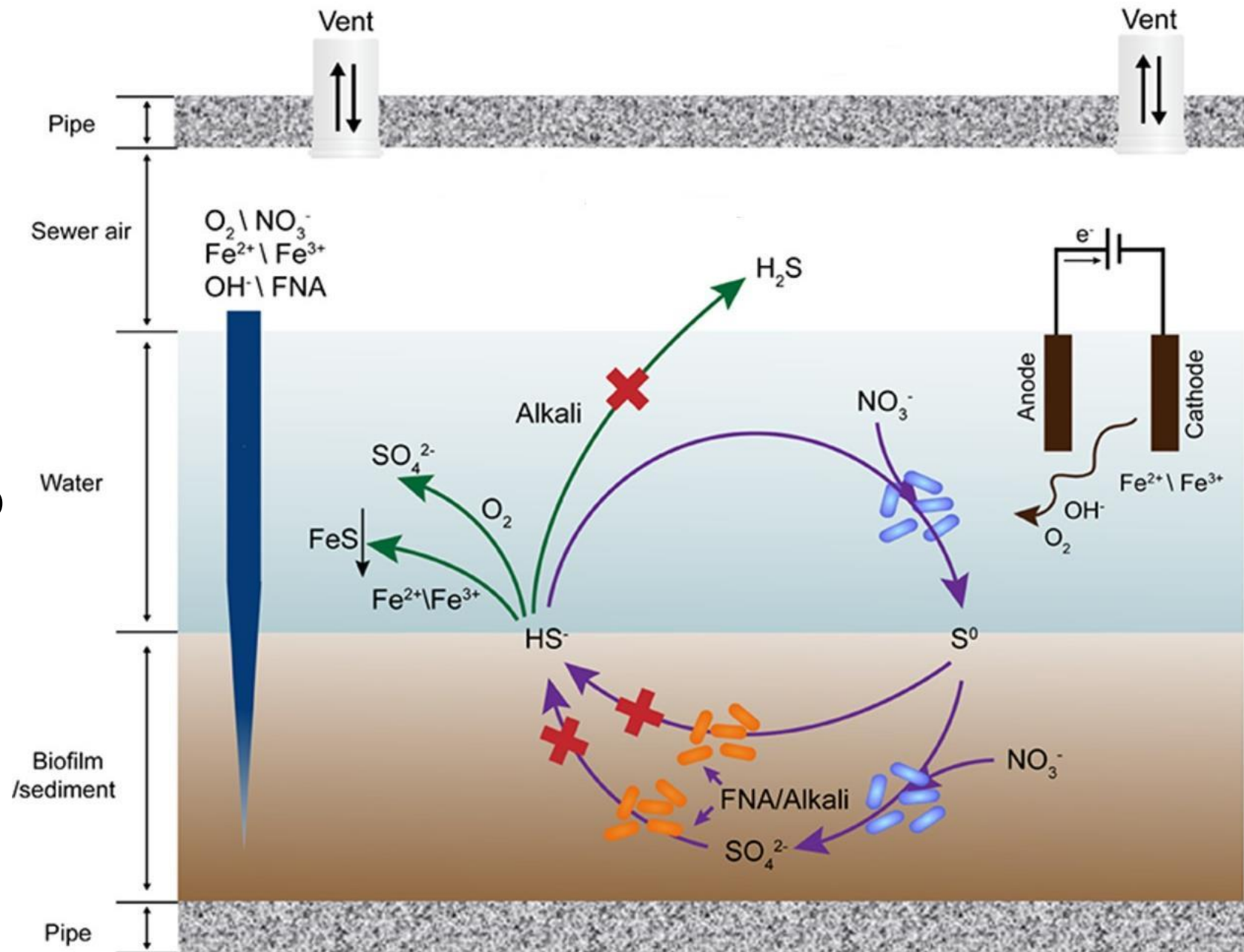


# Hvilken vej viser forskningen?

Nye lovende teknologier til kontrol/håndtering af svovlbrinte i afløbssystemer





# Forskning i $H_2S$ i afløbssystemer

Ifølge Microsoft AI:

# Et kig i bakspejlet...

---

- Hvor kommer vi fra og hvor er udviklingen på vej hen?



# 1895 - Svovlbrinteproblemer erkendes

- I 1900 beskrev Olmsted og Hamlin<sup>1</sup> hvordan kalbaseret mørtel var svulmet op til dobbelt tykkelse og havde mistet sin styrke omkring et spildevandsudløb i Los Angeles.
- Forfatterne konkluderede efter grundige undersøgelser at "...the corrosive or destructive agent is sulphuric acid"

1. Olmsted, F.H. and H. Hamlin (1900), *Converting portions of the Los Angeles outfall sewer into a septic tank*, *Engineering News*, 44(19), 317-318.

## Engineer Makes 6-Mile Sewer Voyage

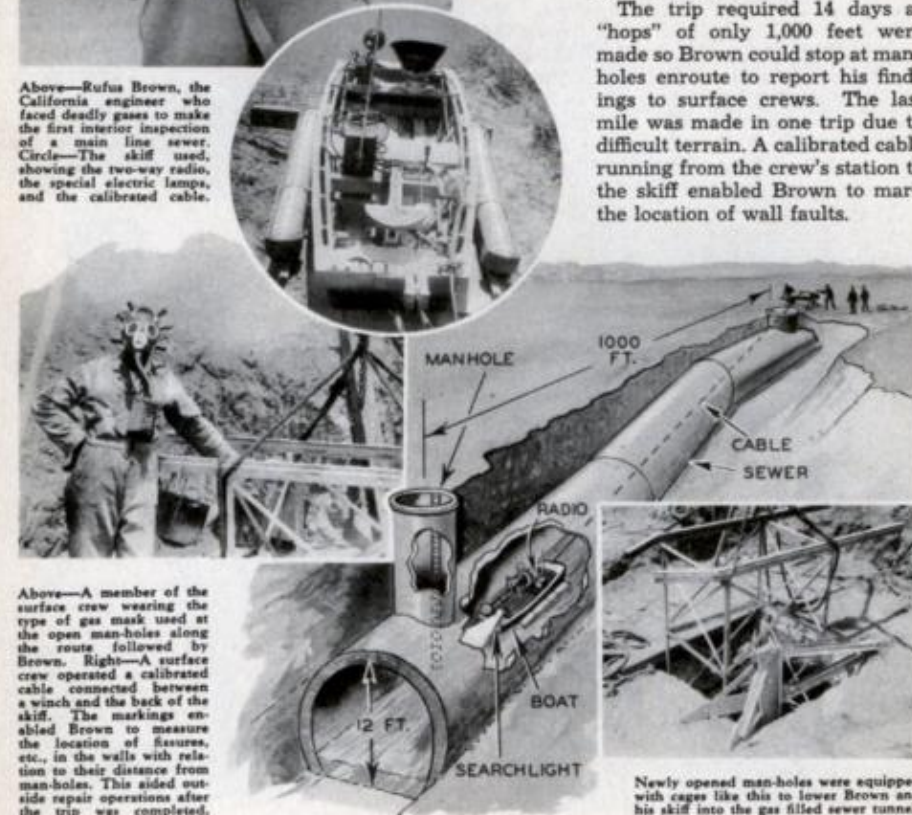


Above—Rufus Brown, the California engineer who faced deadly gases to make the first interior inspection of a main line sewer. Circle—The skiff used, showing the two-way radio, the special electric lamps, and the calibrated cable.

A SIX-MILE trip through deadly gases in the North Outfall sewer in Los Angeles, Calif., was made by Rufus Brown, assistant superintendent of sewers. The hazardous trip was made to determine the condition of the tunnel walls which had been exposed to the sewer's powerful erosive gases since 1922. It was the first inspection trip ever made of the interior of a main sewer line.

A special unsinkable skiff that was propelled by the swift flow of the sewer stream was used. It carried special lights, a two-way radio, a camera and photoflood bulbs. Heavily insulated electric wiring was used to offset the possibility of a spark causing an explosion of the sewer gases. Brown wore a rubber suit fitted with an oxygen mask and a two-hour oxygen supply tank.

The trip required 14 days as "hops" of only 1,000 feet were made so Brown could stop at man-holes enroute to report his findings to surface crews. The last mile was made in one trip due to difficult terrain. A calibrated cable running from the crew's station to the skiff enabled Brown to mark the location of wall faults.

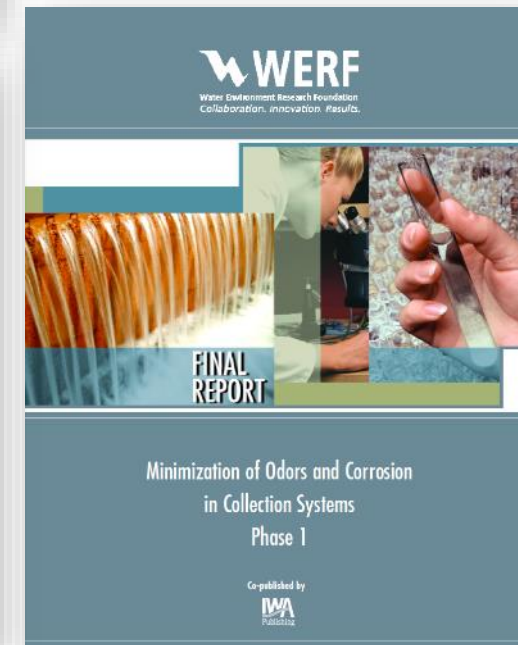
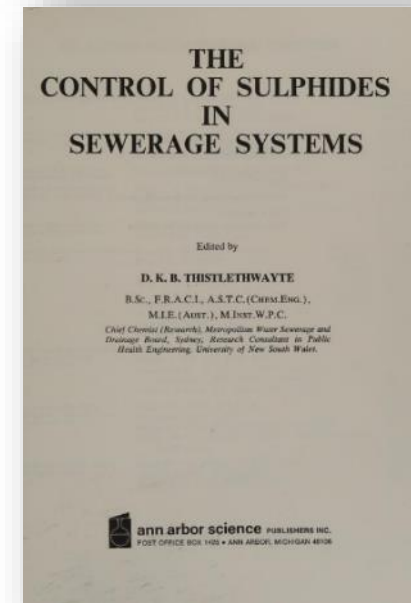
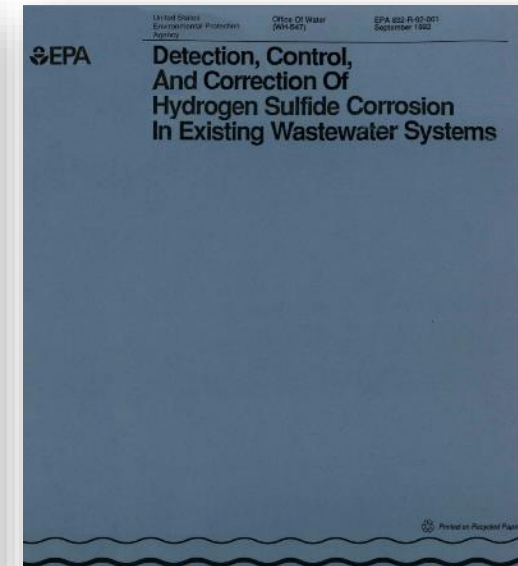
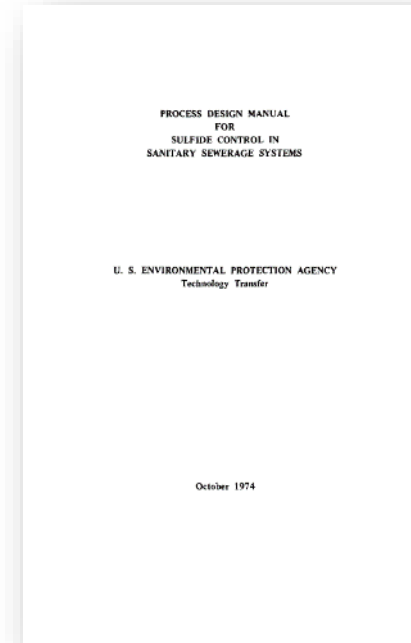


Above—A member of the surface crew wearing the type of gas mask used at the open man-holes along the route followed by Brown. Right—A surface crew operated a calibrated cable connected between a winch and the back of the skiff. The markings enabled Brown to measure the location of fissures, etc., in the walls with relation to their distance from man-holes. This aided outside repair operations after the trip was completed.

Newly opened man-holes were equipped with cages like this to lower Brown and his skiff into the gas filled sewer tunnel.

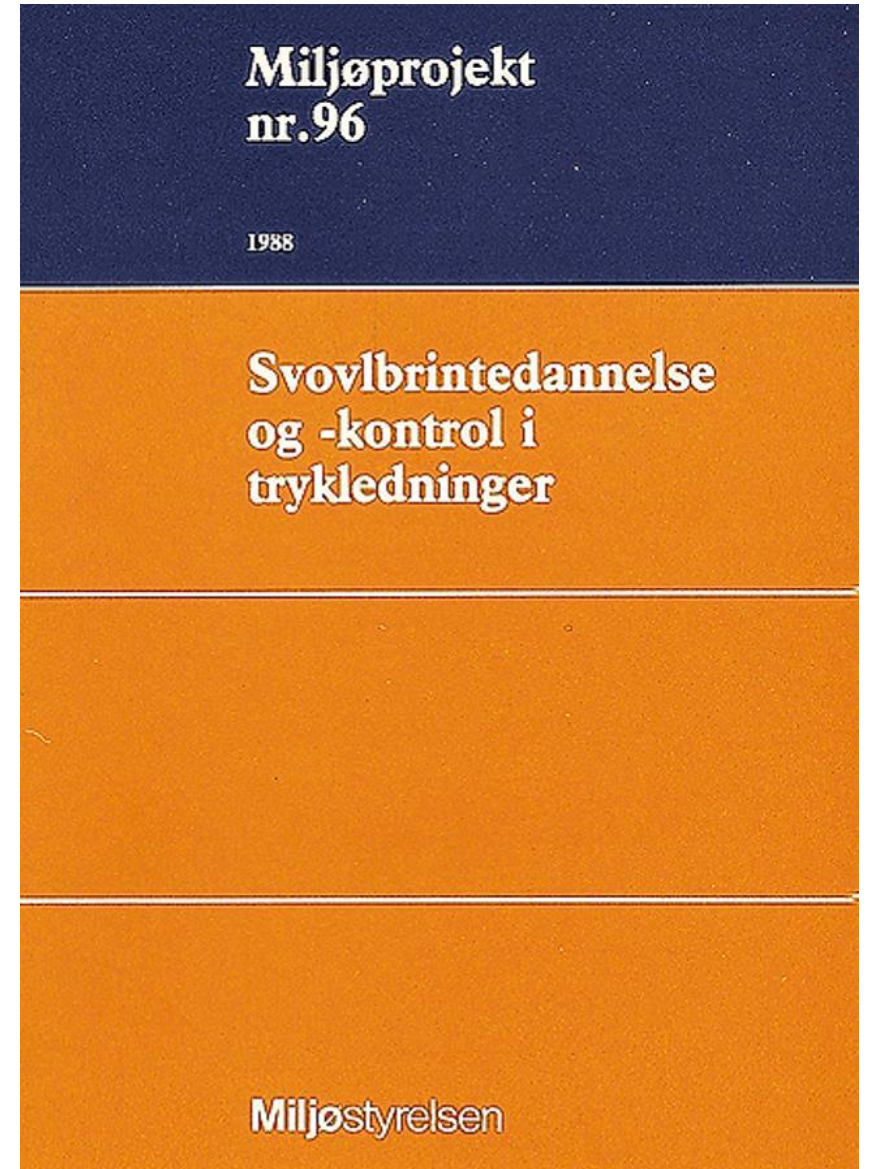
# 19XX

- I gennem det 20. århundrede blev der forsket i svovlbrinte problemer i en række lande og flere design manualer o.l. blev udgivet
- Primært i lande som USA, Sydafrika og Australien



# Udviklingen herhjemme

- I 1988 udgav Miljøstyrelsen projektrapporten ”Svovlbrintedannelse og -kontrol i trykledninger”, som dels beskrev baggrunden for problemerne og som også gennemgik en række metoder til bekæmpelse af svovlbrinte.
- I de efterfølgende år foregik der et stort forsknings- og udviklingsarbejde – særligt på AAU



# 2010 →

- I de senere år har flere forskningsgrupper arbejdet intensivt med problemstillinger relateret til svovlbrinte – særligt:
  - Australien, University of Queensland
  - Australien, UNSW Sydney
  - Tyskland, TU Berlin
  - Belgien, Universiteit Ghent
  - ...

## Sewer Corrosion and Odour Research (SCORE) Project



The SCORE project was a five-year (12/2008 – 11/2013), \$21M research project jointly funded by the Australian government (\$4.7M) and many major water utilities in Australia. This was likely the largest ever research project worldwide focusing on sewer corrosion and odour.



# Et kig i krystalkuglen

---

Hvilke lovende teknologier bliver der forsket i?





# Udvalgte nye metoder

---

- Elektrokemiske metoder
  - Dannelse af fældningskemikalier
  - Magnetite nano-partikler
  - In situ dannelse af O<sub>2</sub>
- Kemidosering
  - Free Nitrous Acid (Saltpetersyrlig)
  - Free Ammonia
  - Jernholdigt vandværksslam
- Biologisk og kemisk H<sub>2</sub>S rensning (end-of-pipe)

# Elektrokemisk H<sub>2</sub>S bekæmpelse

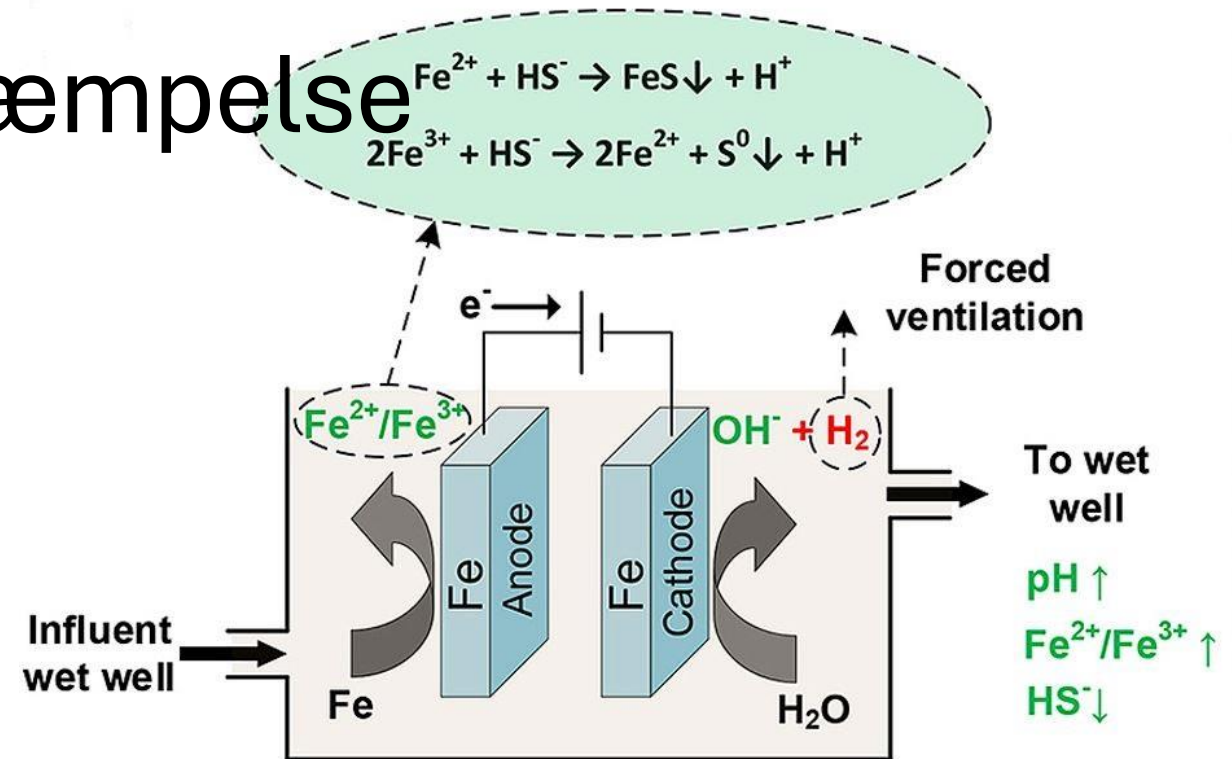
- Elektrokemisk oxidation (iltning) af jernelektroder frigiver Fe<sup>2+</sup> som udfælder svovlbrinte

- **Fordele:**

- Ingen sure opløsninger
- Højere effektivitet end kemi-dosering

- **Ulemper**

- Tunge elektroder som skal skiftes
- Temperatur-afhængig process
- Sidereaktioner kan danne uønskede gasser (H<sub>2</sub>, Cl<sub>2</sub>,...)



Forsøgsopstilling fra Frejlev ifbm CLEAN projekt

# Visuelle observationer

- ▶ Udfældet jern adsorberes til overflader i opstillingen
- ▶ Jern oxideres til  $\text{Fe}^{3+}$  og udfælder som jernoxid/hydroxid (rust/okker)
  - Dette kan enten ske på elektroden eller via reaktion med ilt ( $\text{O}_2$ ) fra atmosfæren.
  - Hovedparten af jernoxidationen elektroderne resulterer i  $\text{Fe}^{2+}$  dannelse (effektivitet var cirka 90%)



# Fuldskala forsøg

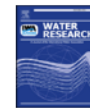
- Konfiguration af kulstofstålpladerne i den elektrokemiske celle; 2x50 kulstofstålplader.
- Elektrokemisk celle under drift, dvs. dækket af et PVC-låg for at ventilere den producerede brintgas ( $H_2$ ) ud i atmosfæren.



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Water Research

journal homepage: [www.elsevier.com/locate/watres](https://www.elsevier.com/locate/watres)



Full-scale investigation of in-situ iron and alkalinity generation for efficient sulfide control

Ilje Pikaar <sup>a,b,\*</sup>, Markus Flugen <sup>a</sup>, Hui-Wen Lin <sup>c</sup>, Sirajus Salehin <sup>a,b</sup>, Jiuling Li <sup>b</sup>, Bogdan C. Donose <sup>d</sup>, Paul G. Dennis <sup>e</sup>, Lisa Bethke <sup>b</sup>, Ian Johnson <sup>f</sup>, Korneel Rabaej <sup>b,g</sup>, Zhiguo Yuan <sup>b</sup>

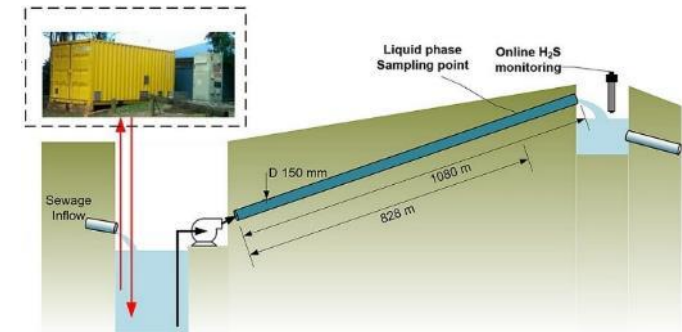
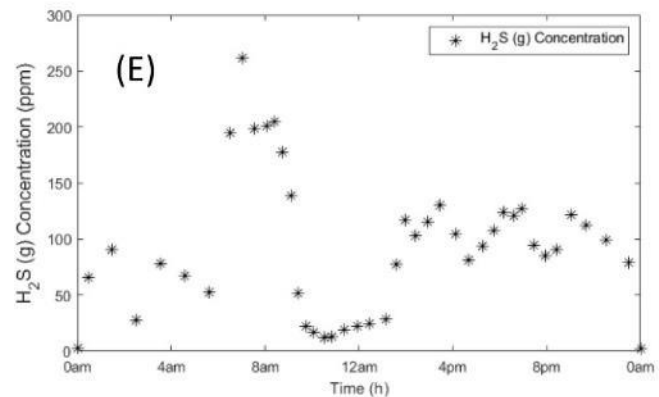
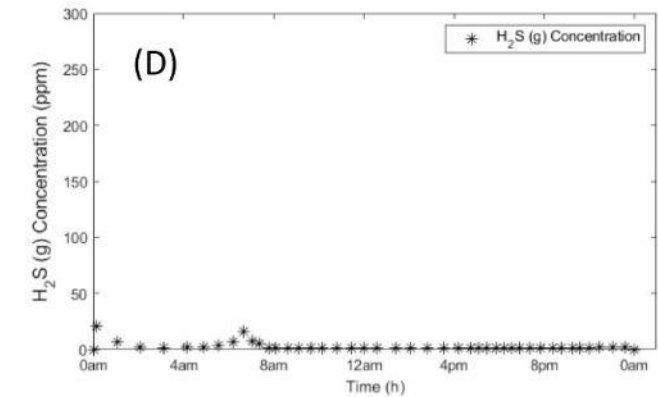
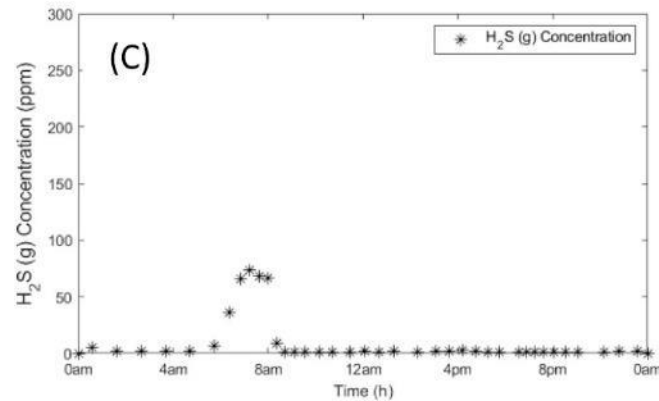
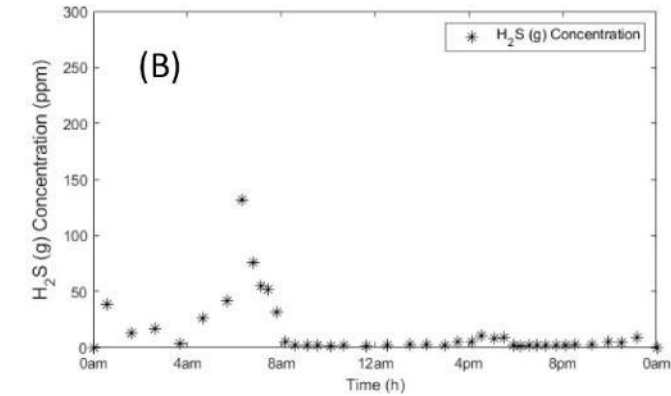
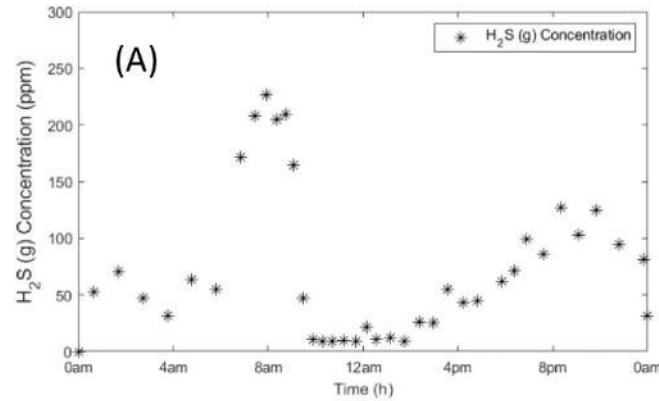


<https://doi.org/10.1016/j.watres.2019.115032>



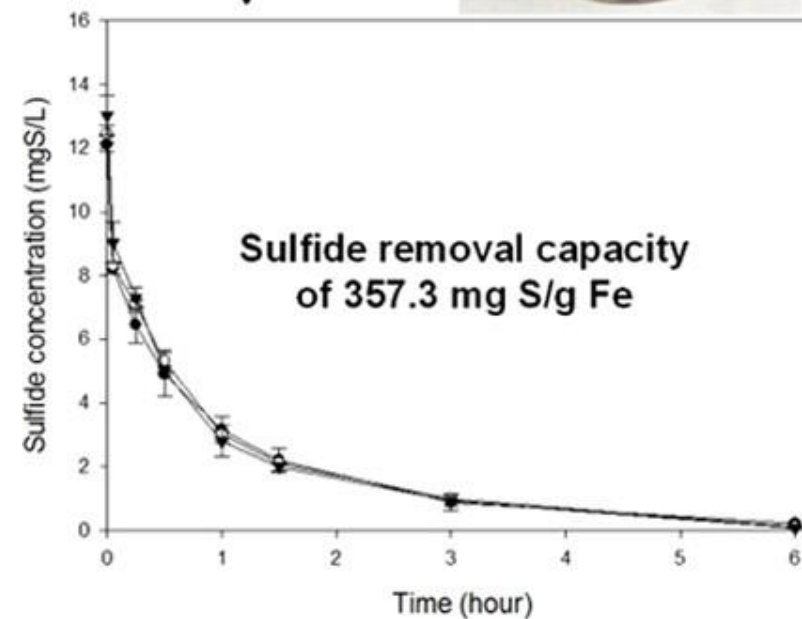
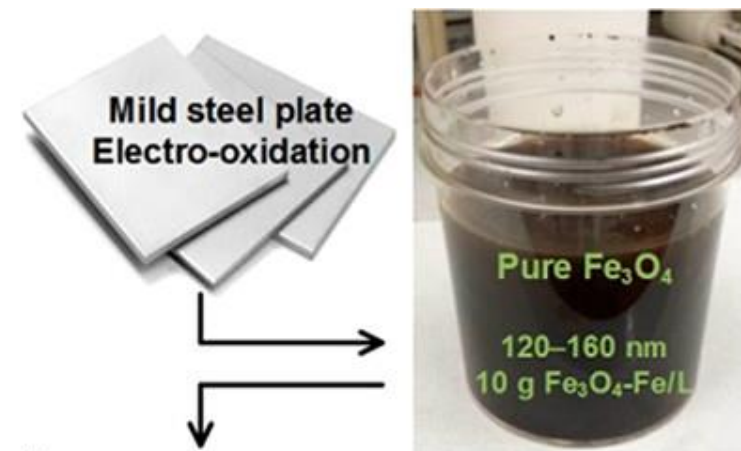
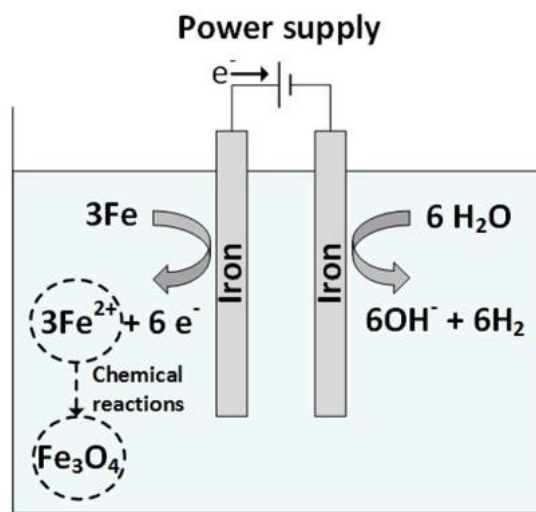
# Elektrokemisk $H_2S$ bekæmpelse

- Resultater fra fuldskala test i Holland
- A: Baseline
- B – D: Forsøgsperiode med hhv 80, 120 og 160 A strømstyrke under pumpning
- E: Efter forsøgsperiode



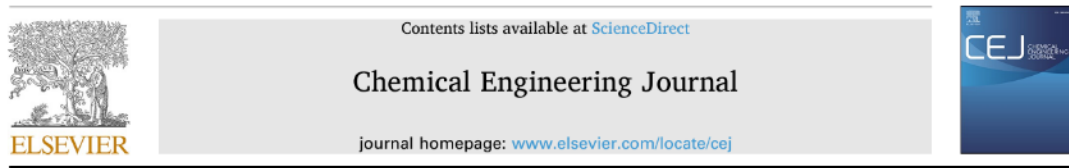
# Elektrokemisk dannelse af magnetite NP

- Magnetite nano-partikler (120-160 nm) dannes ved oxidation af jernelektroder i elektrolytvæske
- H<sub>2</sub>S fjernelse ved adsorption (hurtig) og efterfølgende oxidation (langsom)



# Nye metoder baseret på elektrokemi

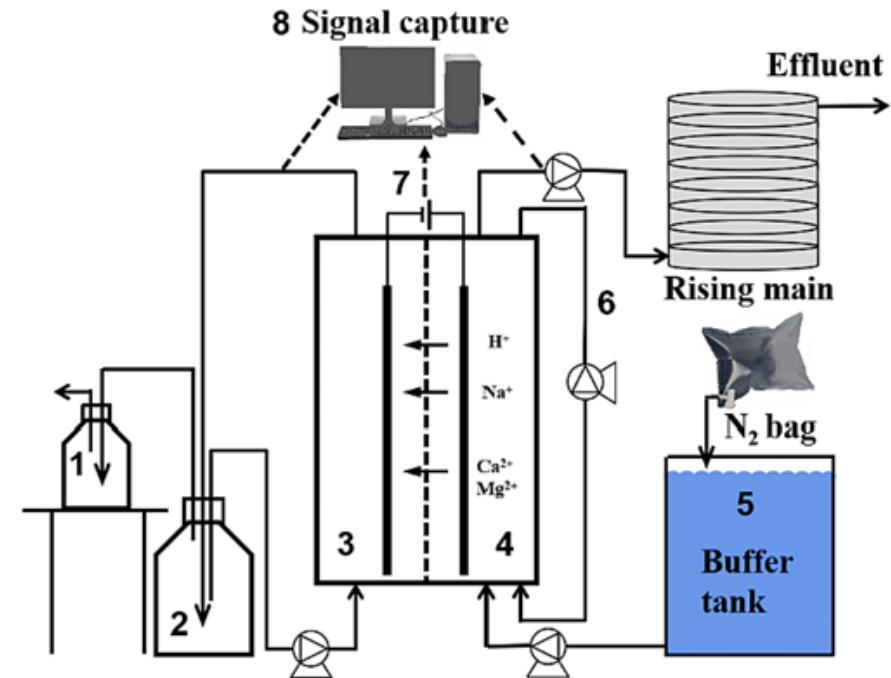
- *In-situ* O<sub>2</sub> dannelse i trykledninger



*In-situ* oxygen generation using Titanium foam/IrO<sub>2</sub> electrode for efficient sulfide control in sewers

Jiaqi Hou, Yiming Li, Haixiao Guo, Yufen Wang, Yanying He, Tingting Zhu\*, Yiwen Liu\*

School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, PR China



- |                                   |                             |
|-----------------------------------|-----------------------------|
| 1 cathode water-lock (0.1 M NaOH) | 5 buffer tank (20 L)        |
| 2 cathode external buffer (0.1 L) | 6 anodic recirculation flow |
| 3 cathode                         | 7 direct current power      |
| 4 anode                           | 8 signal capture            |

**Fig. 1.** The schematic diagram of experimental setup. The sewage is constantly flowing from the buffer tank into the anode chamber and getting mixed with oxygen in the anode chamber. Afterward, it flows out through a rising main. The electrolyte in the cathode chamber is circulated and any hydrogen production is discharged through a water-lock device, while preventing the entry of carbon dioxide.

# Resultater

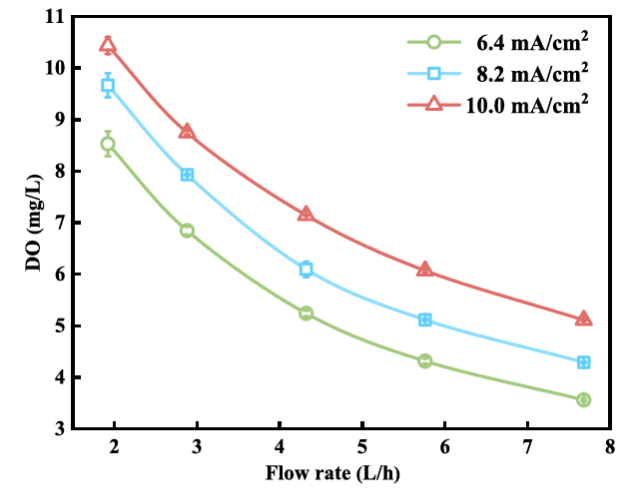


Fig. 3. Typical profiles of DO concentrations in the anode effluent at various current densities of 6.4, 8.2 and 10 mA cm<sup>-2</sup> with anode flow rates of 1.92, 2.88, 4.32, 5.76 and 7.68 L/h.

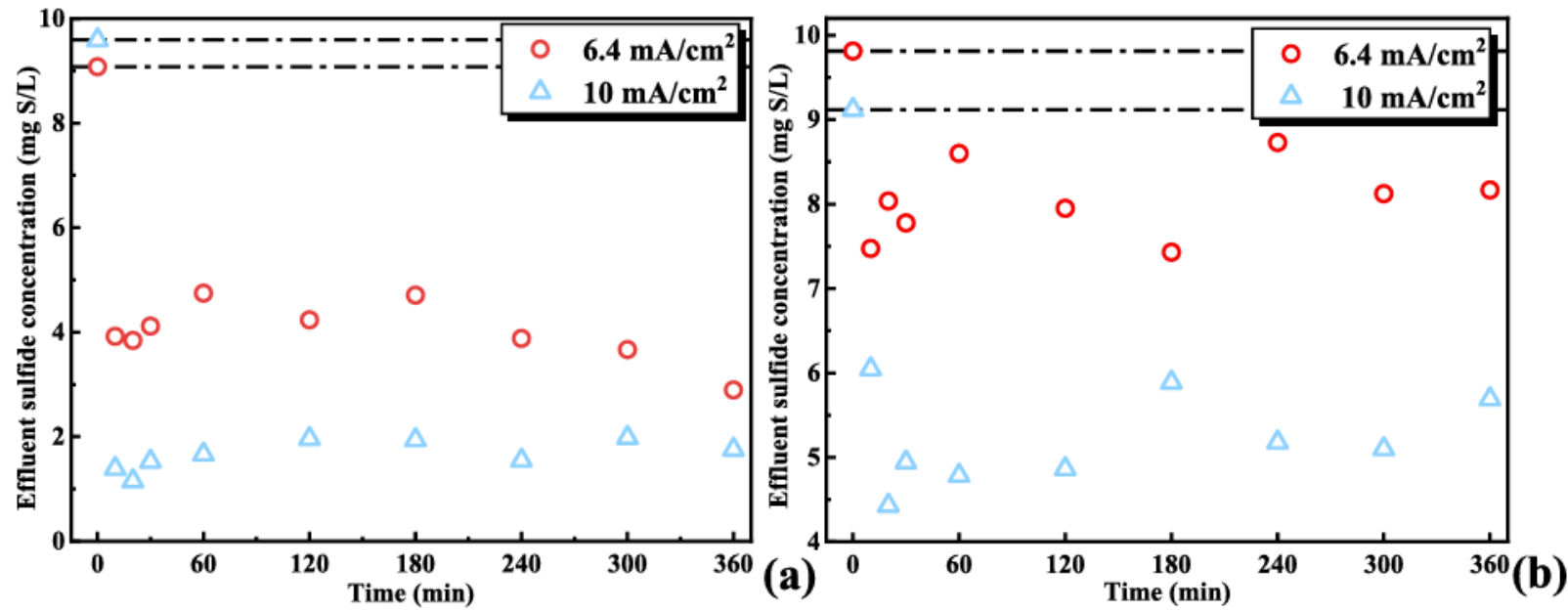
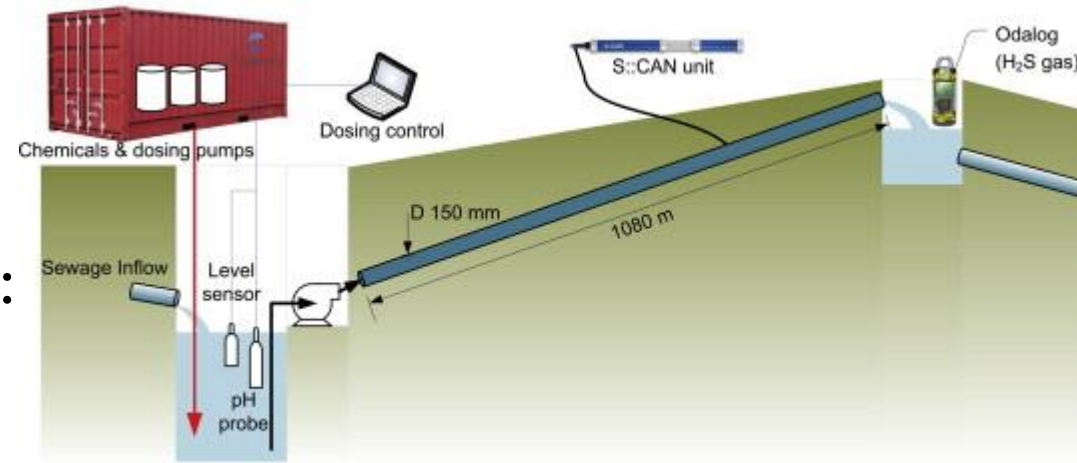


Fig. 4. The effluent sulfide concentrations at current densities of 6.4 and 10 mA cm<sup>-2</sup> with a flow rate of (a) 2.88 L/h or (b) 5.76 L/h in the absence of trace elements during 6 h experiments.

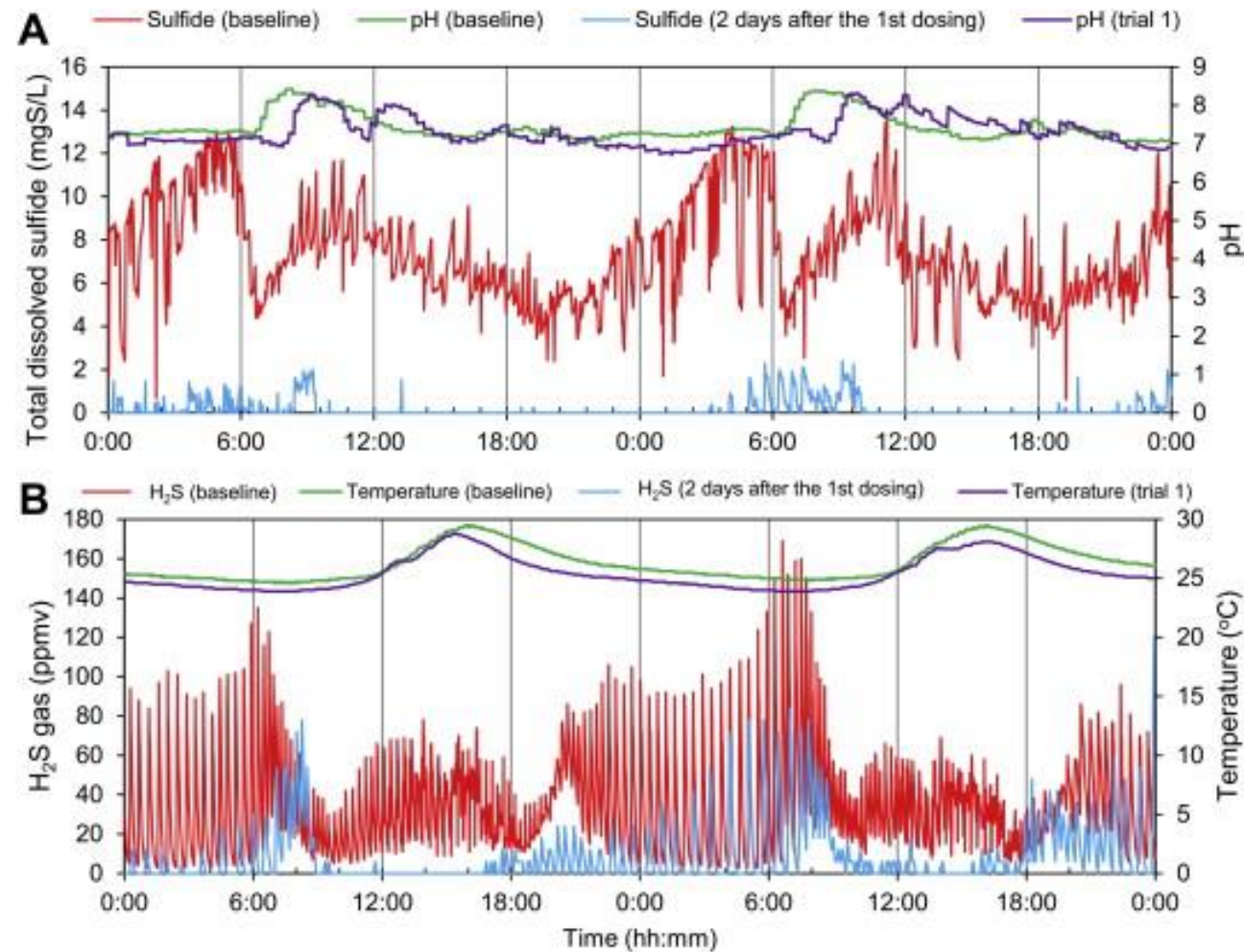


# Free Nitrous Acid (FNA)

- Lovende teknologi som har været testet igennem en række år
- Free Nitrous Acid (Da.: Saltpetersyrting  $\text{HNO}_2$ ) er toksisk for sulfatreducerende mikroorganismer
- Tilføres periodisk i pumpeump:
- $\text{pK}_a = 3.4$
- Typisk dosis for effektiv kontrol:  
100 mg-N/L @ pH 6



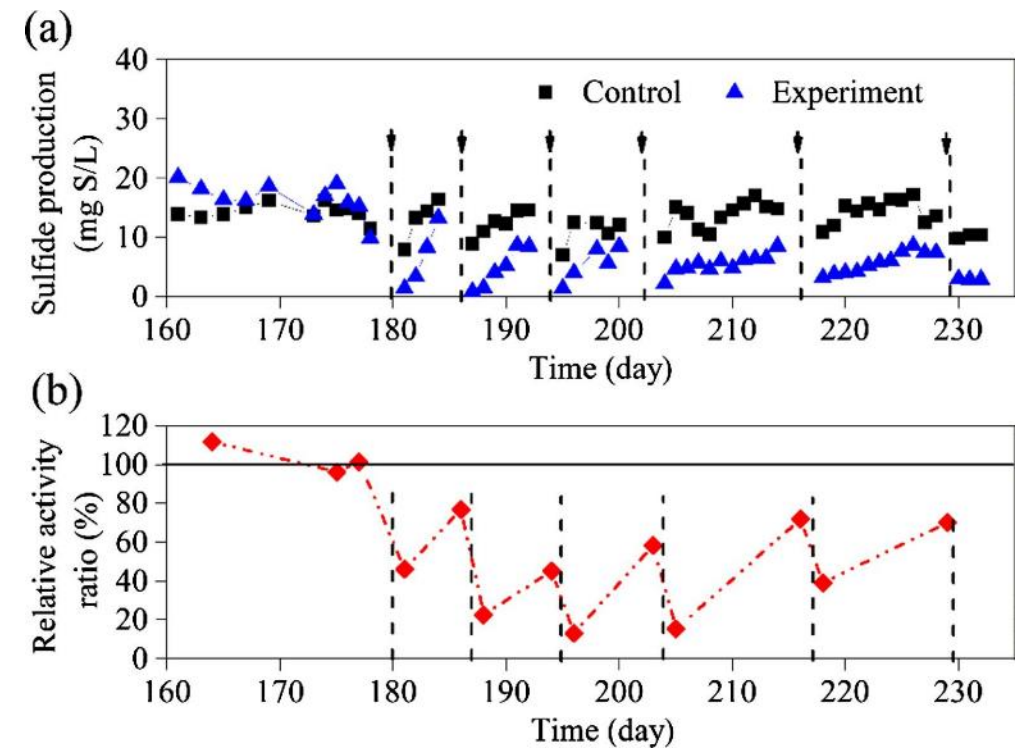
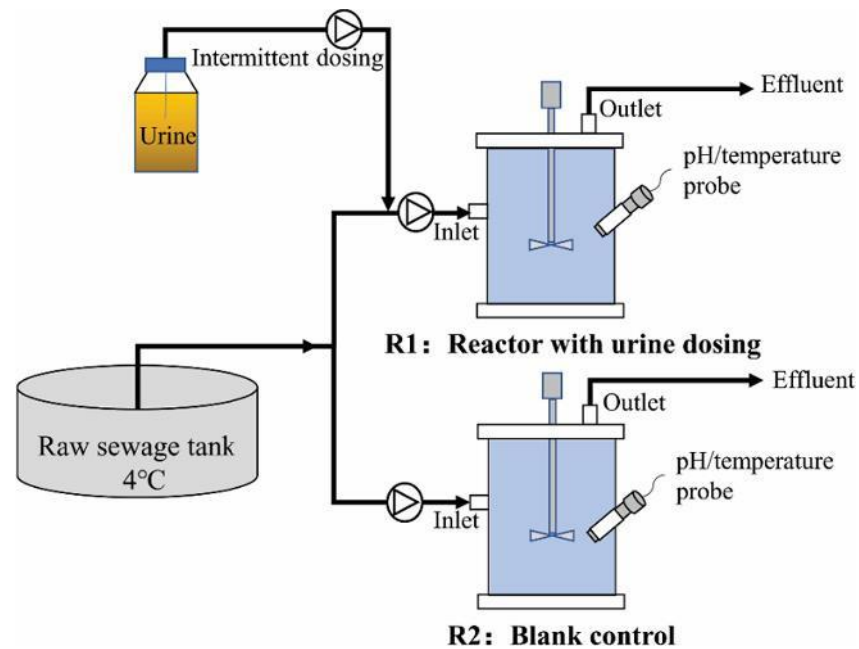
# FNA



*Typical profiles of dissolved sulfide and wastewater pH at 828 m downstream of a pump station before and after dosing (A); and H<sub>2</sub>S gas and atmospheric temperature in discharge wet well before and after dosing (B).*

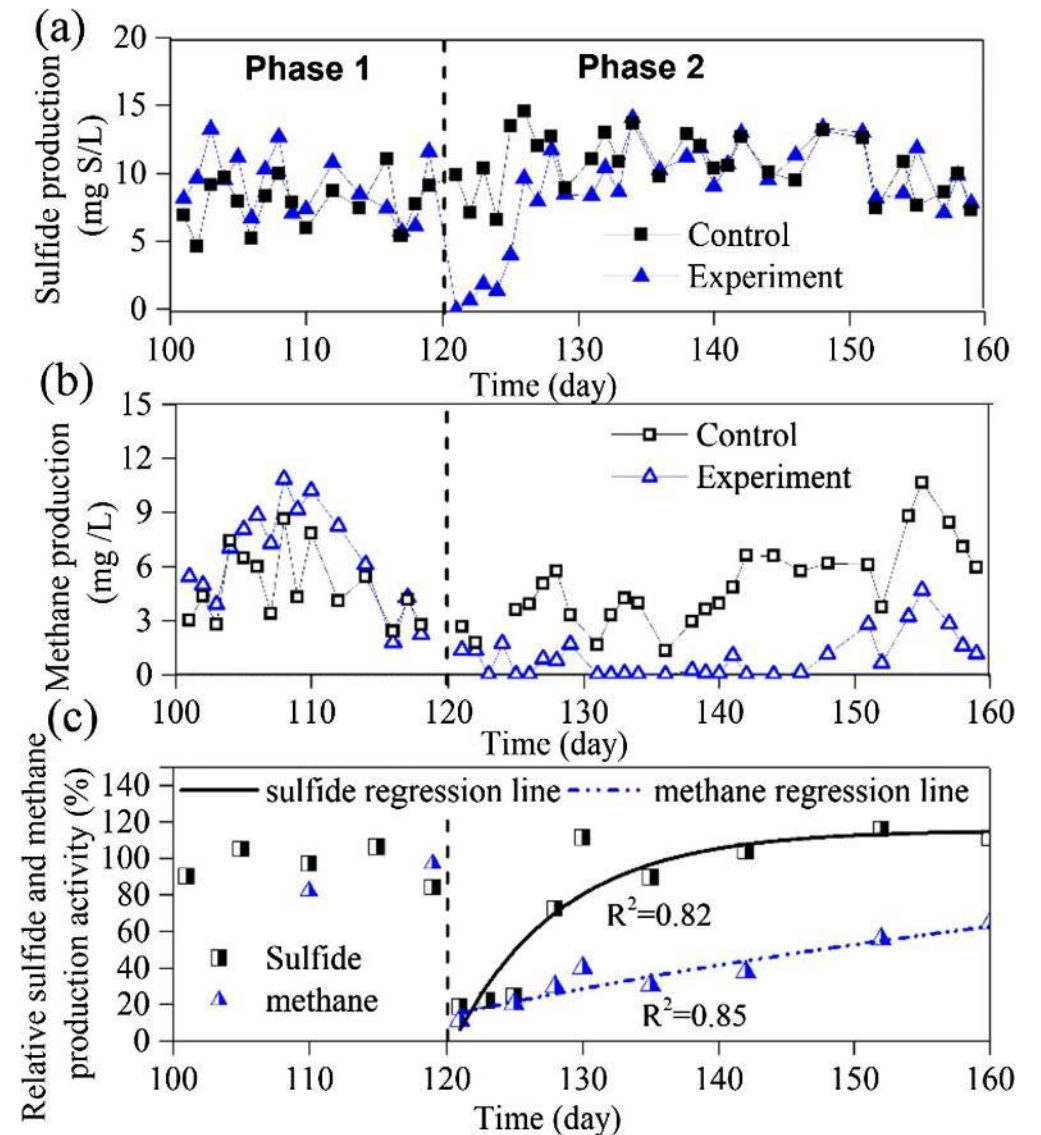
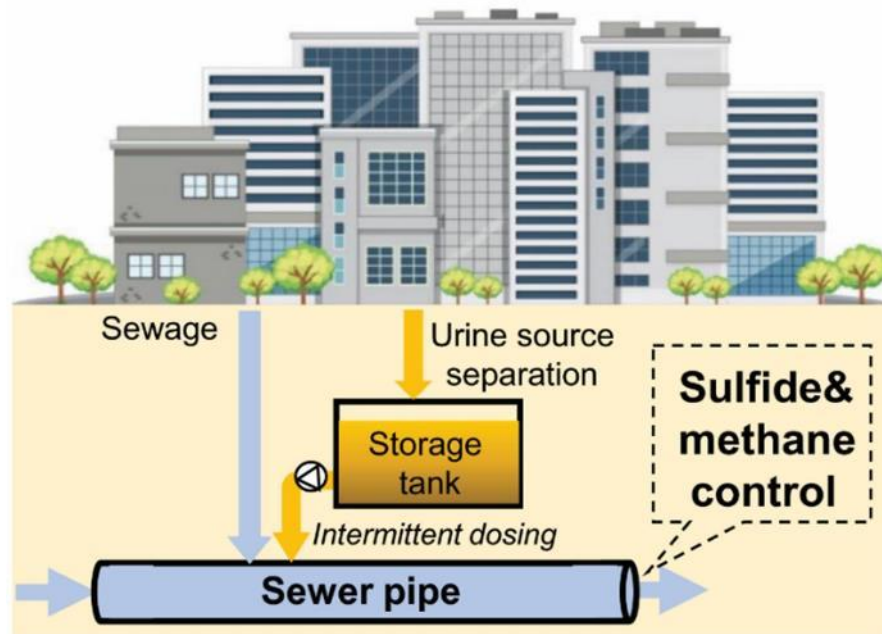
# Free Ammonia (FA)

- Høje koncentrationer af ammonium/ammoniak er inhiberende for sulfat reducerende bakterier (SRB)

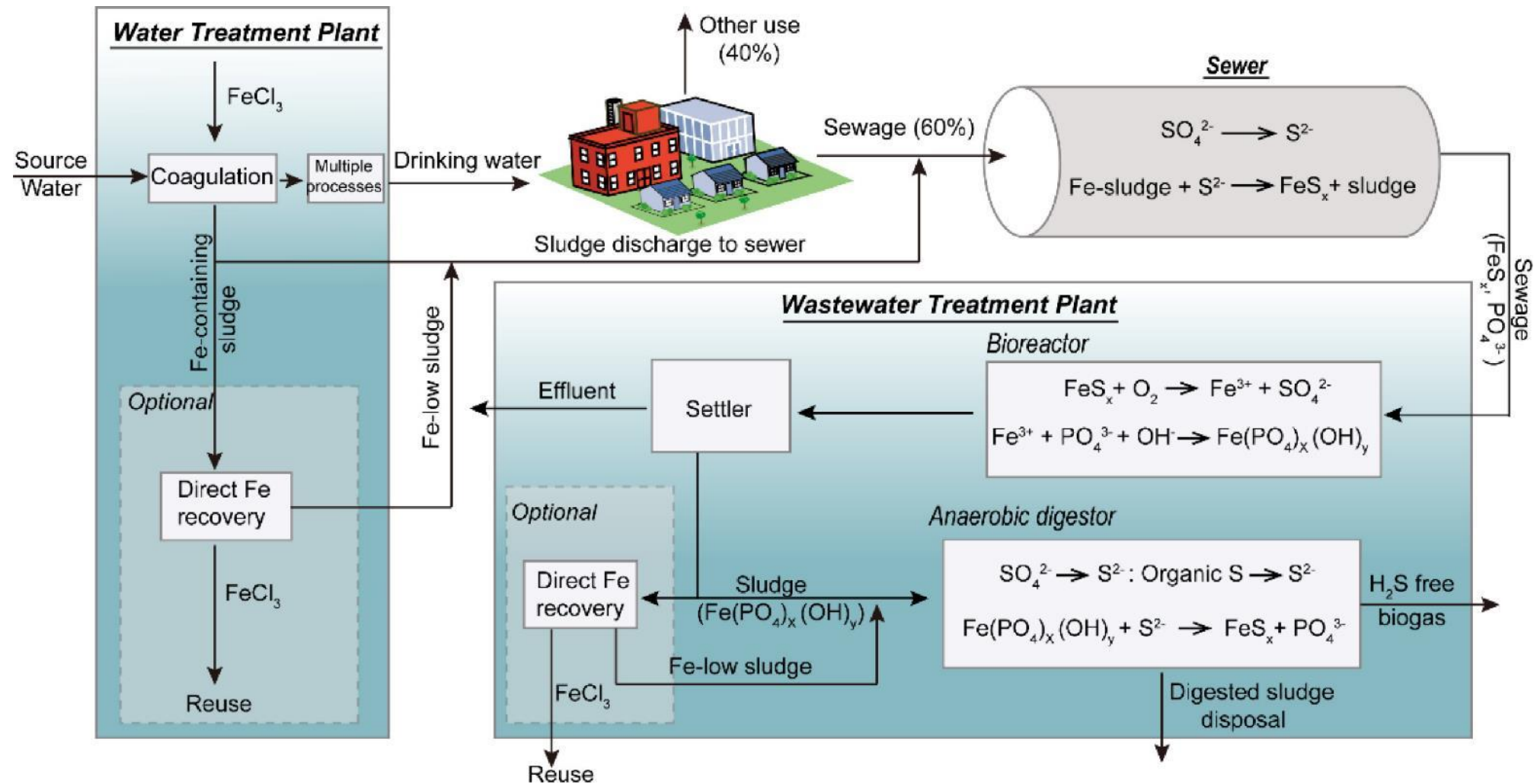


# Free Ammonia (FA)

- Særligt metan-dannelsen reduceres

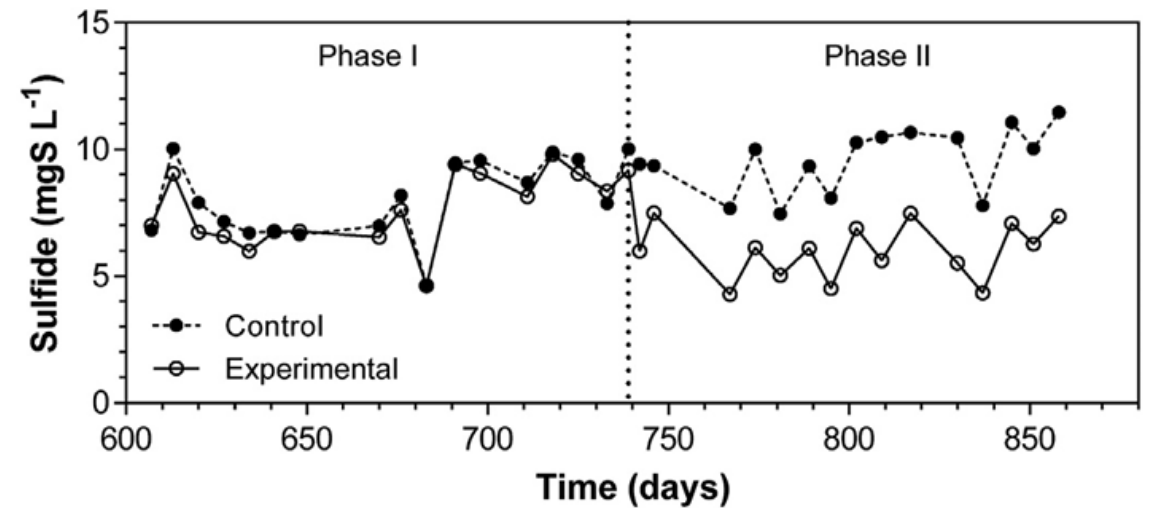


# Jernholdigt slam fra drikkevandsproduktion



Jernslam doseret i underskud, men stadig en positiv effekt

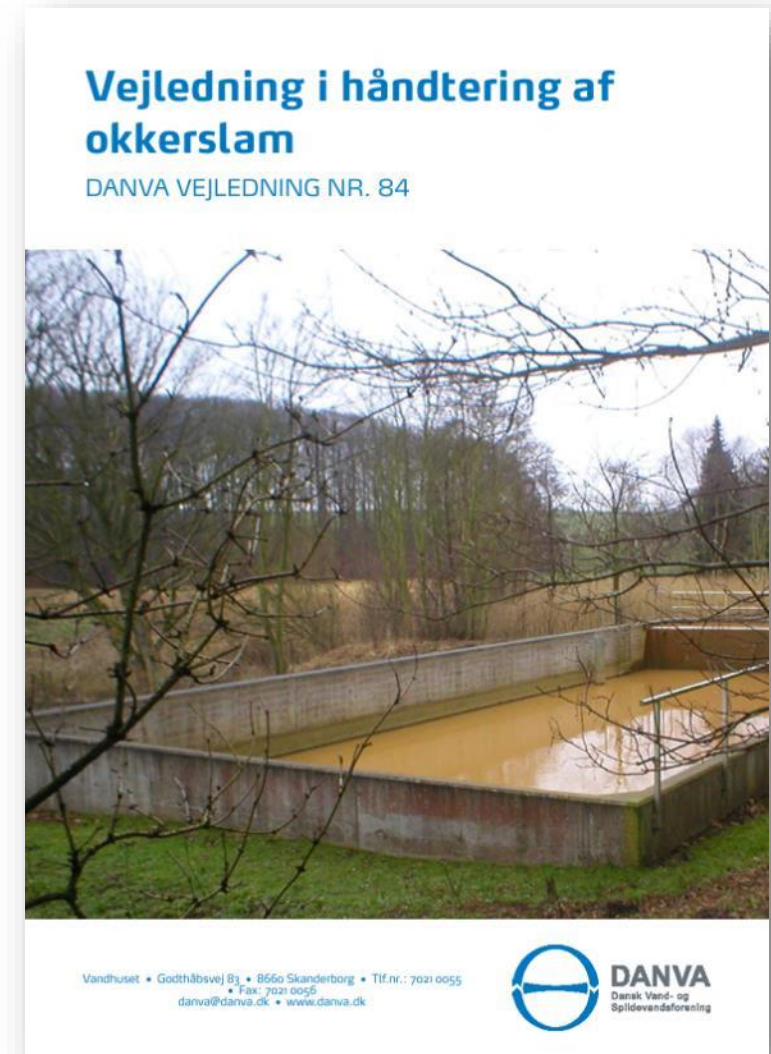
## Jernholdigt slam fra drikkevandsproduktion



**Fig. 2.** Dissolved sulfide concentrations of the control and experimental sewer reactor effluents (see Fig. 1, sample point 2). Phase I is the baseline period. The vertical dotted line (Day 739) marks when in-sewer iron-rich DWS dosing to the Experimental system (Phase II) was initiated.

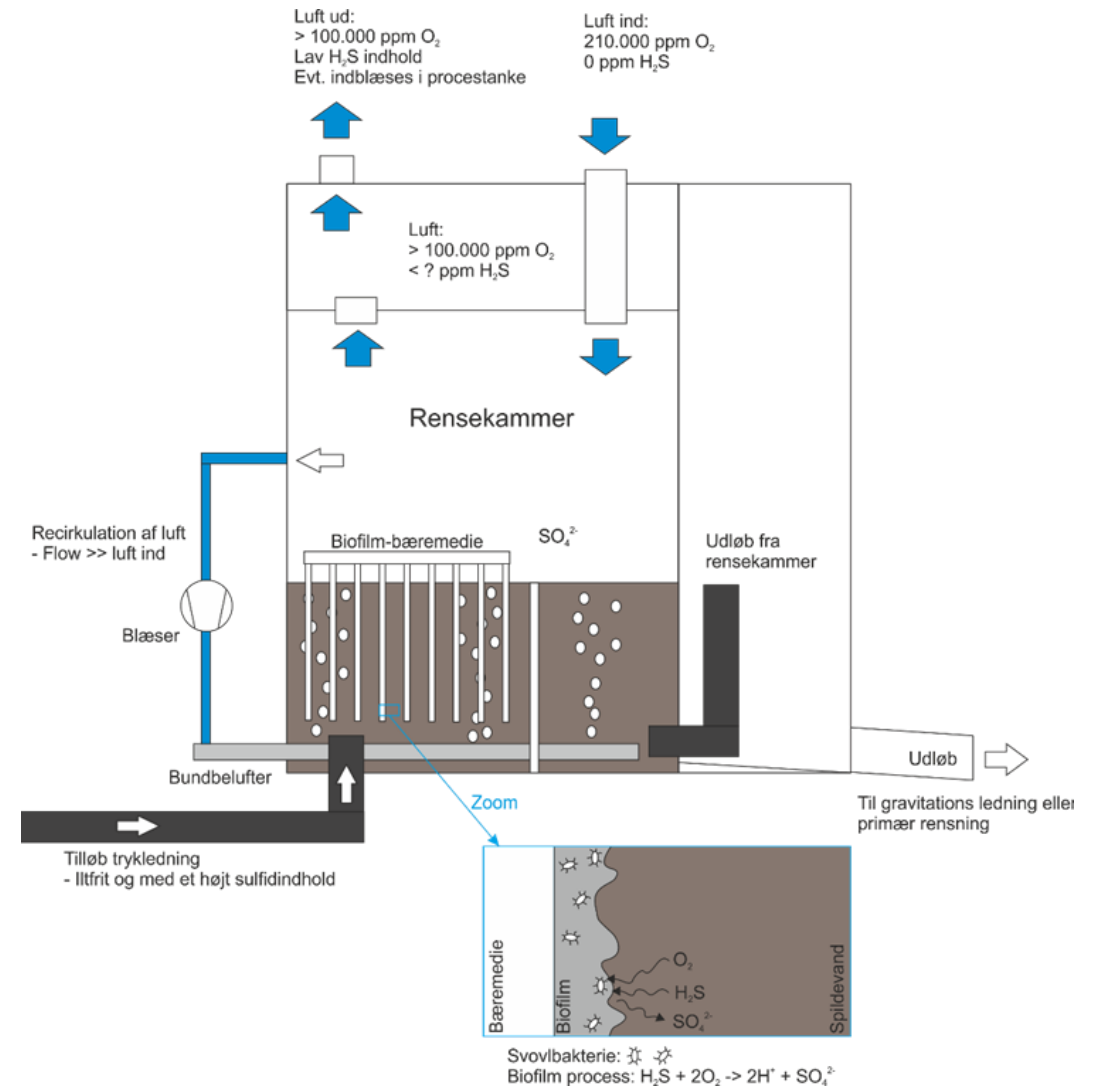
# Jernholdigt slam fra drikkevandsproduktion

- Anvendelsen er afprøvet i flere omgange herhjemme
- Anvendes også i biogas-anlæg til at reducere H<sub>2</sub>S indhold
- Der er en række udfordringer, som dog kan løses/håndteres
  - Indhold af tungmetaller, fx As
  - Varierende jernindhold
  - Bundfældning/omrøring nødvendig



# End-of-pipe behandling

- VUDP foreningen har i 2023 bevilliget midler til projektet ”Bæredygtig svovlbrintebehandling i tryksatte afløbssystemer”
- Projektet skal undersøge potentialet for biologisk omsætning af svovlbrinte nedstrøms for (lange) trykledninger

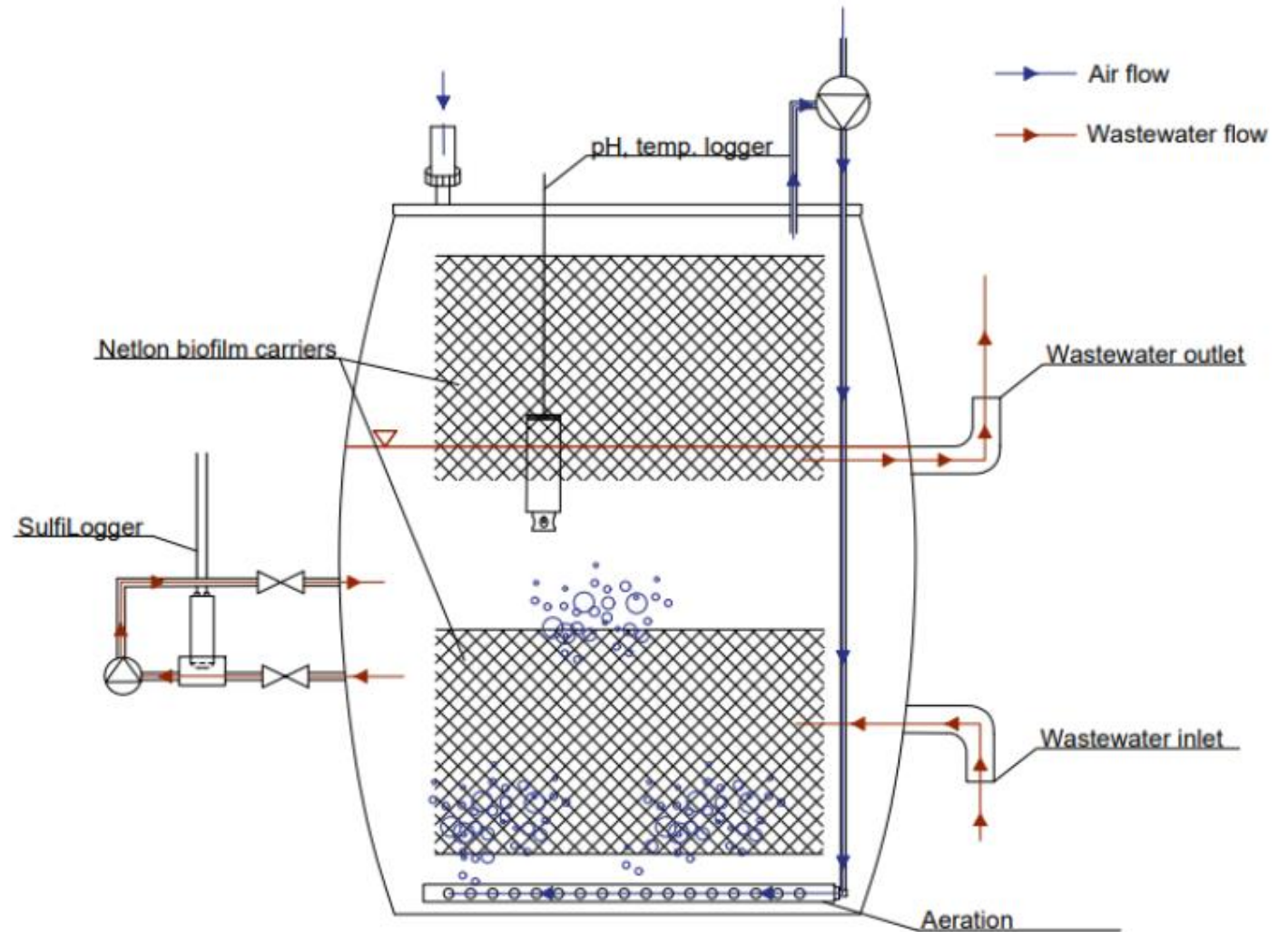




# End-of-pipe behandling

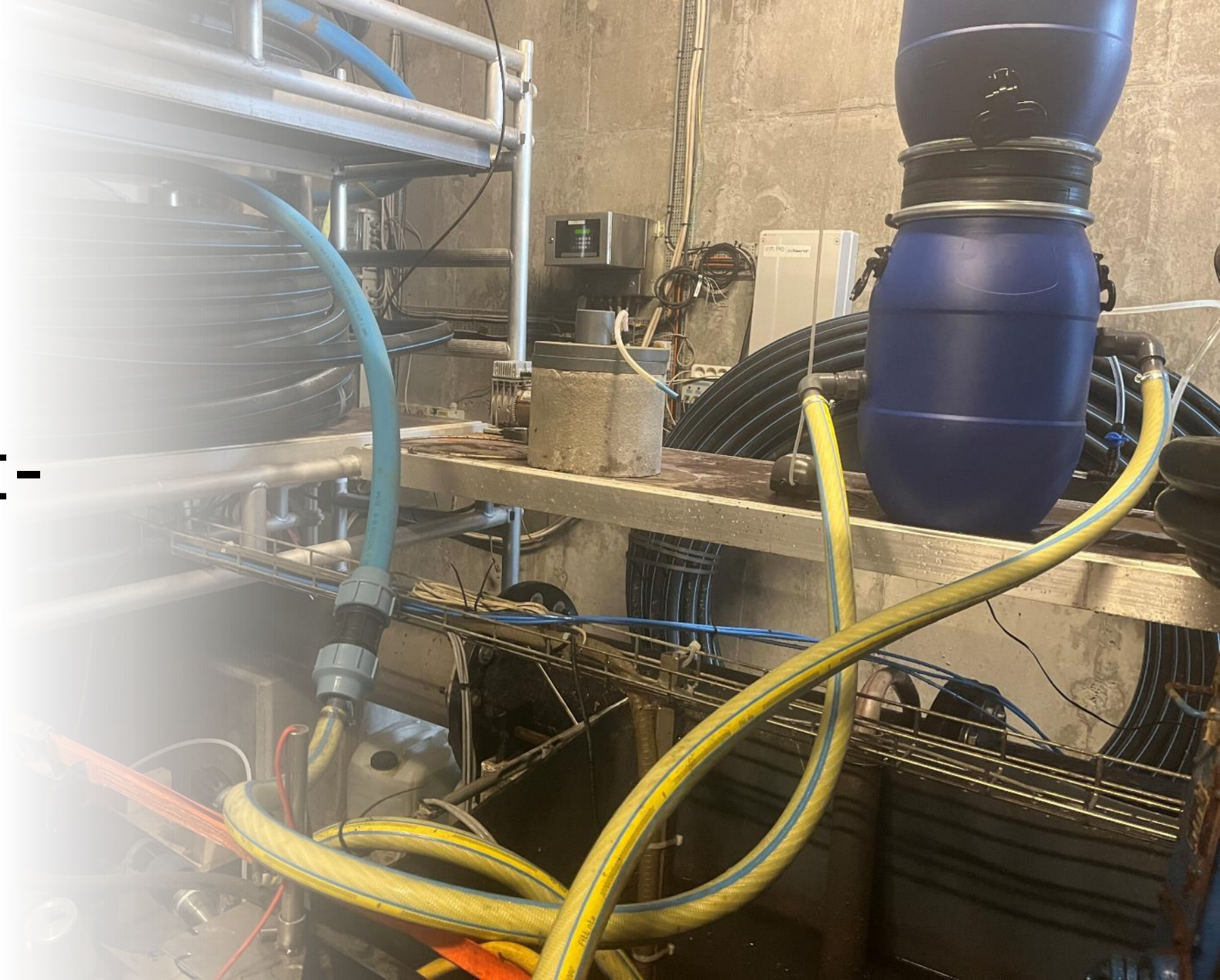
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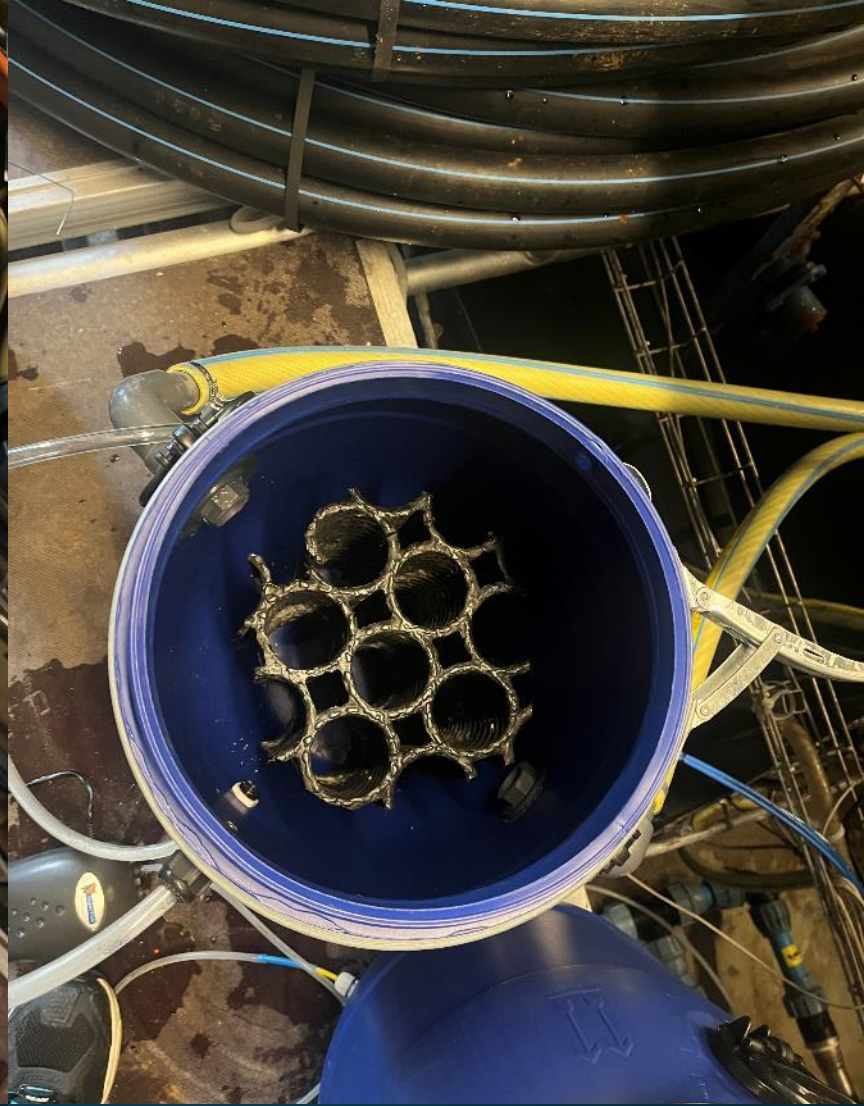
- Projektperiode Sept-23 til Feb-25 (sommer 2025)
- Pilot-skala opstilling er ved at blive testet (30 L opstilling efter en 400 m Ø50 mm trykledning)



# Lille pilot- skala

Forsøgsopstilling



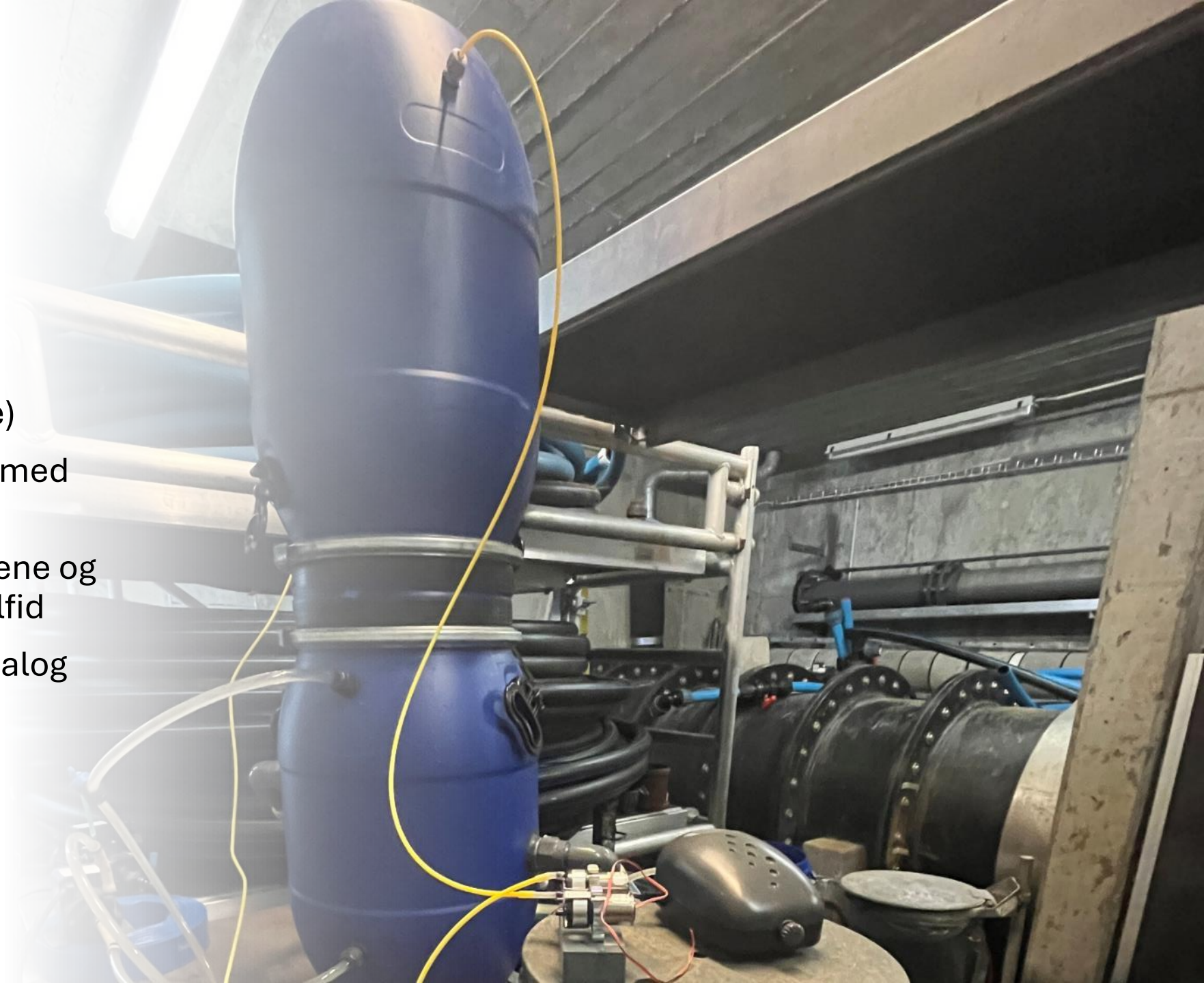


Forsøgsopstilling

Lille pilotskala

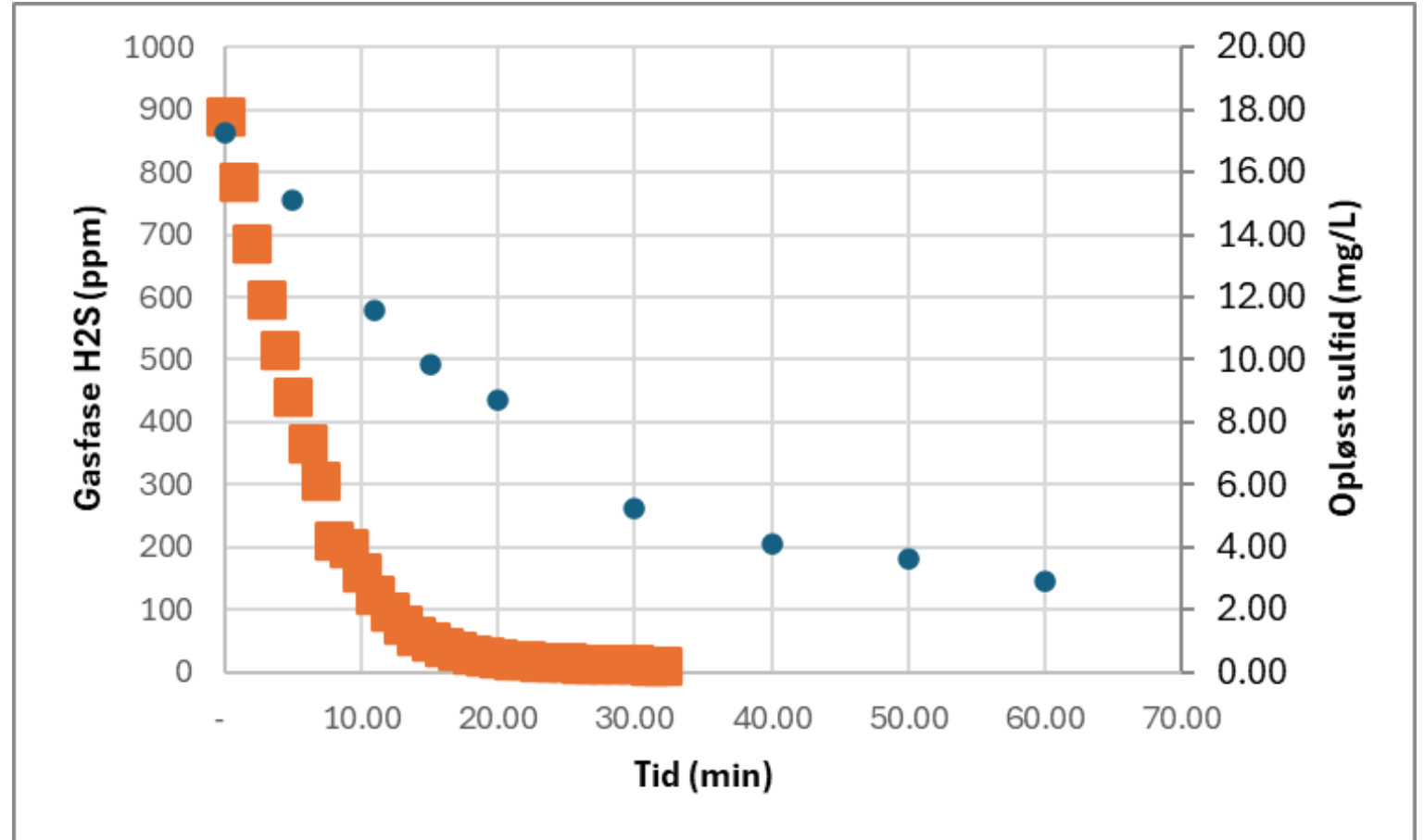
# Forsøg – lille pilotskala

- Luft recirkuleres med luftpumpe (lamelpumpe)
- Spildevand recirkuleres med centrifugalpumpe
- Vandprøver udtages løbene og analyseres for opløst sulfid
- Gas-fase males med Odalog



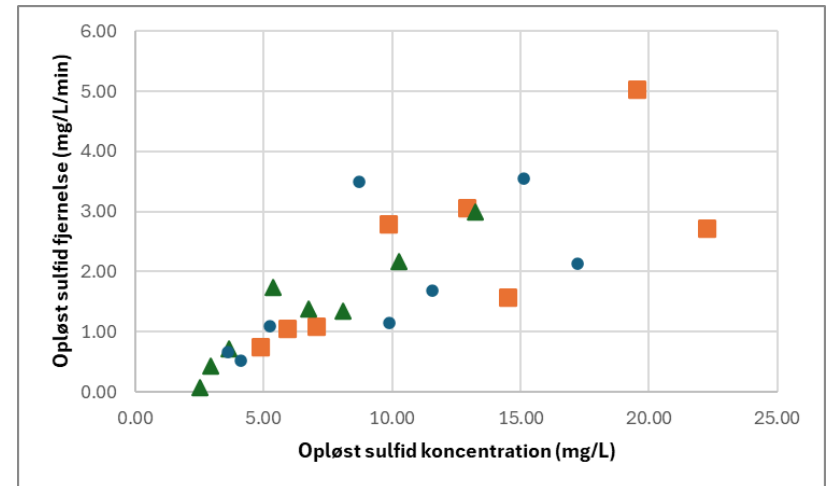
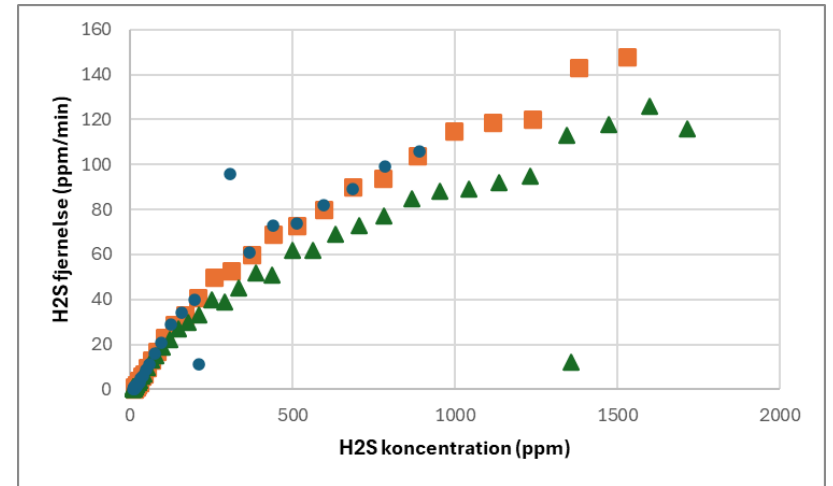
# FORELØBIGE RESULTATER

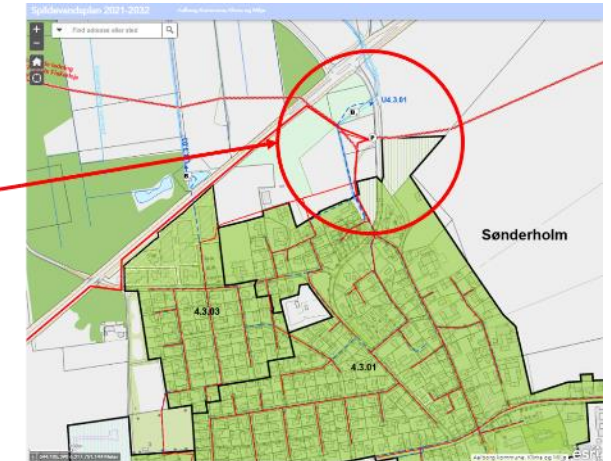
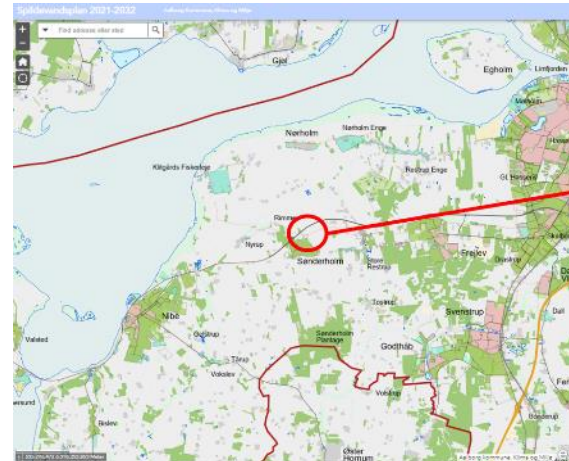
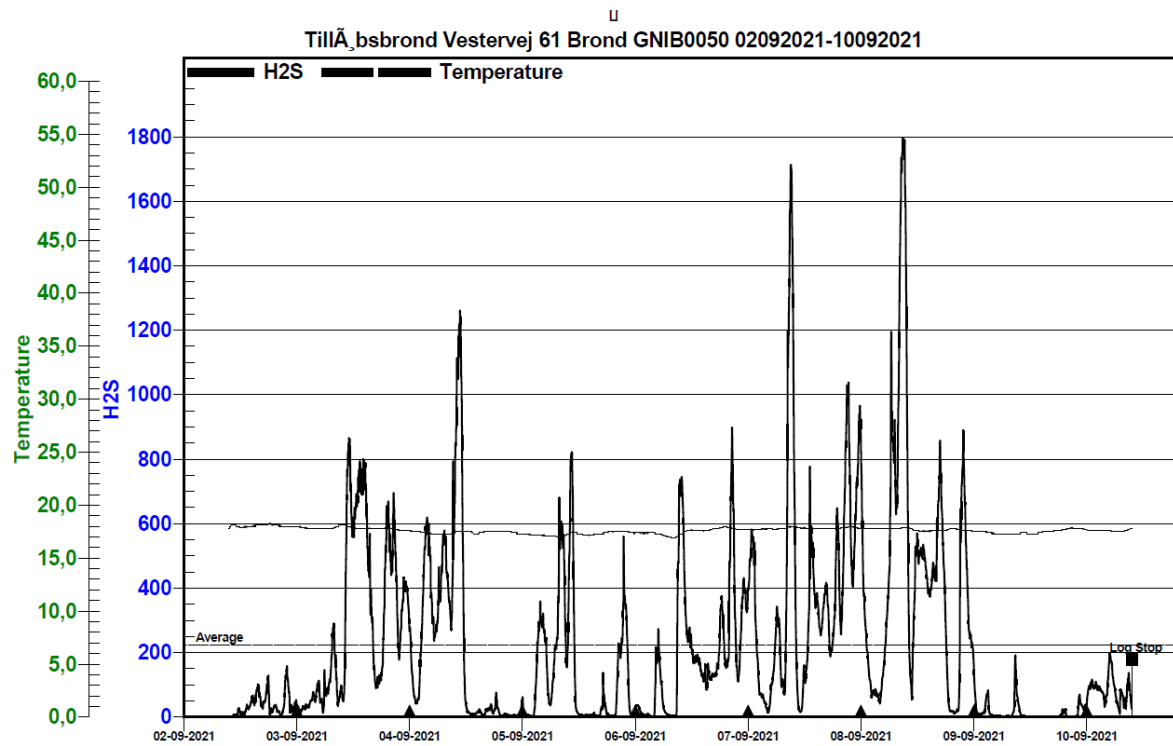
Fjernelse af opløst sulfid:



# Foreløbige resultater

- Hurtig H<sub>2</sub>S fjernelse (halveringstid mindre end 30 min)
- Resultater er stærkt afhængige af beluftningskapacitet > kraftig blæser
- Tidskrævende med kemisk analyse af prøver > on-line måling med sulfilogger





# Stor pilot-skala forsøg

Opstart til ultimo 2024 (der er søgt 3 mdr udsættelse af slutdato. Forsommer 2025).

# Anbefalene strategier

