

Chromium (VI) and vanadium (V) in groundwater: investigating bioremediation solutions

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Microbial reduction of metals

Mainly Cr(VI) and Cr(III)

Chromium (Cr) and vanadium (V) exist as different species:
Cr(VI) and V(V) most toxic and mobile

V(V), V(IV), V(III) and V(II)

Reduction of Cr(VI) and V(V) via (indirect) microbial processes

1. Indirect biological reduction (iron sulfides)

2. Direct biological reduction (electron acceptor)

Site

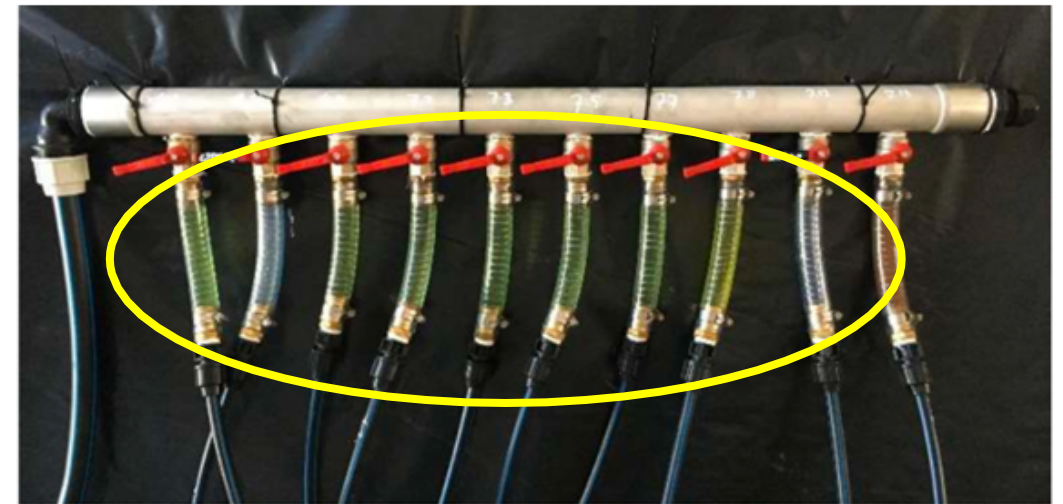
In-situ remediation of cVOC and Cr(VI) contamination at an urban site

- Former galvanizing plant in The Netherlands; urban area + significant part of the contamination is located under a monumental building.
- Concentrations groundwater: ± 1000 mg/L Cr(VI), ± 100 mg/L cVOCs
- Anaerobic in-situ bioremediation: injections of electron donor to dechlorinate cVOCs and reduce Cr(VI) to Cr(III)

Chromium (VI) in-situ remediation

Source treatment

- Circulations system (flushing)
 - 10 filters
 - Extraction strongly contaminated water
 - Infiltration clean water
 - Removal 13 tonnes highly contaminated material
- Direct injections in cellar
 - 18 injection of 8 m³ electron donor solution



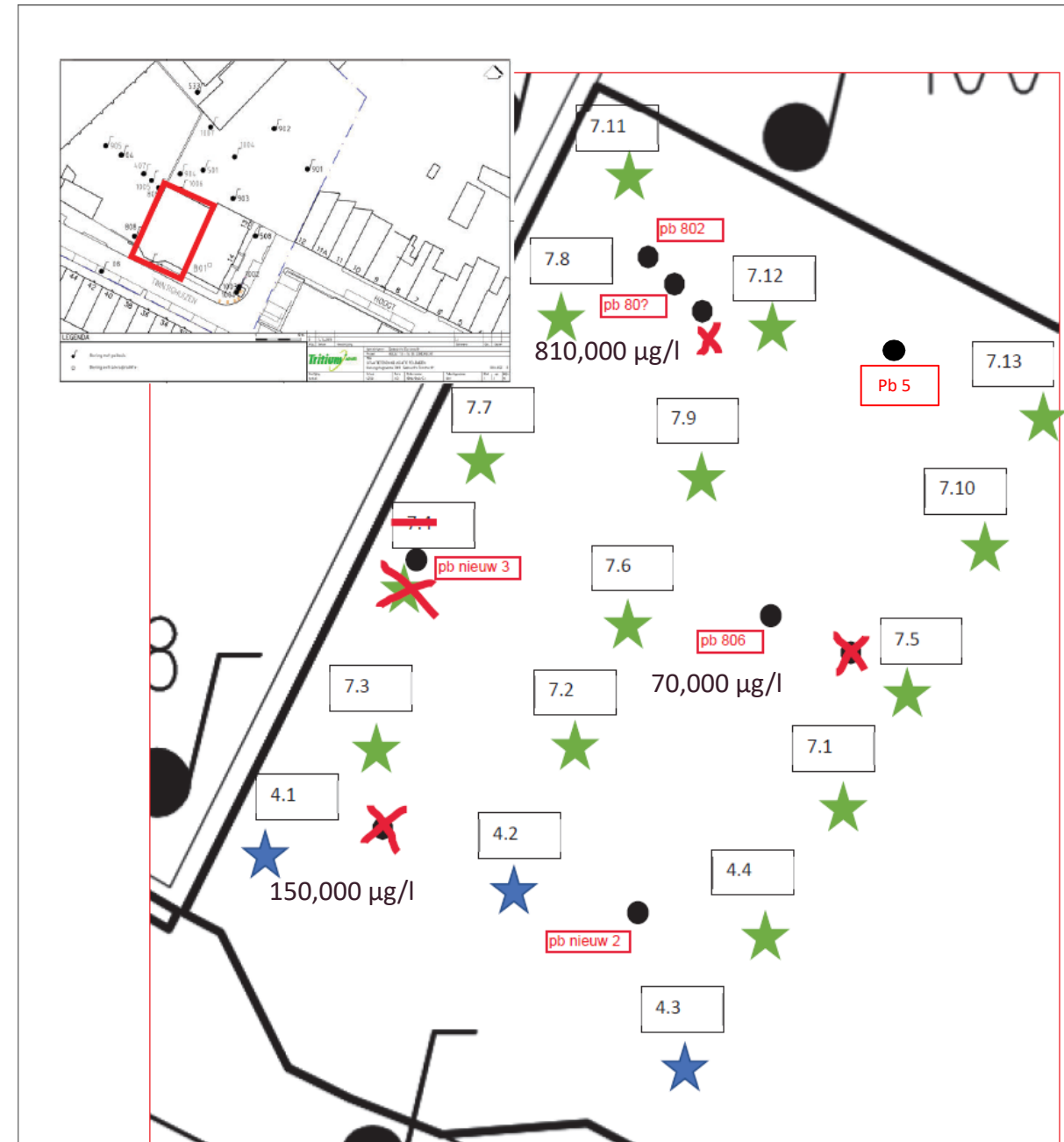
Chromium (VI) in-situ remediation

Treated area

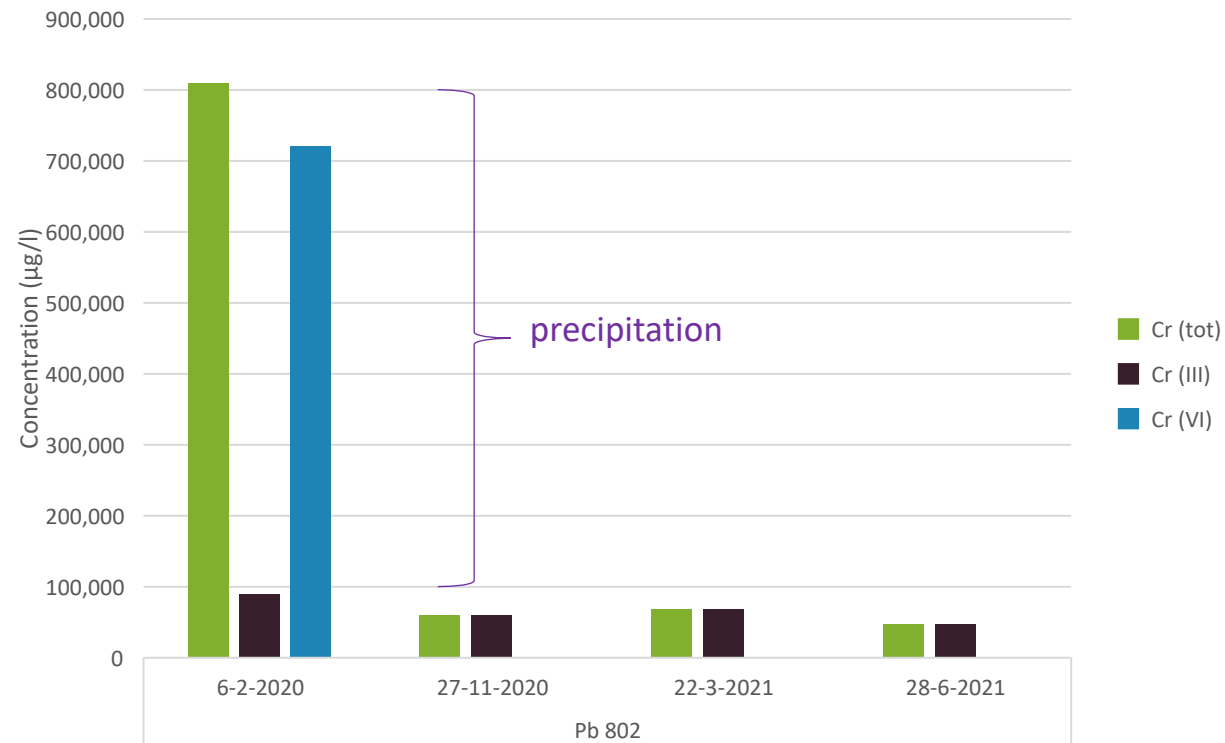
Volume	2,500 m ³
Depth (layer)	7 m-bgl

Max groundwater concentration

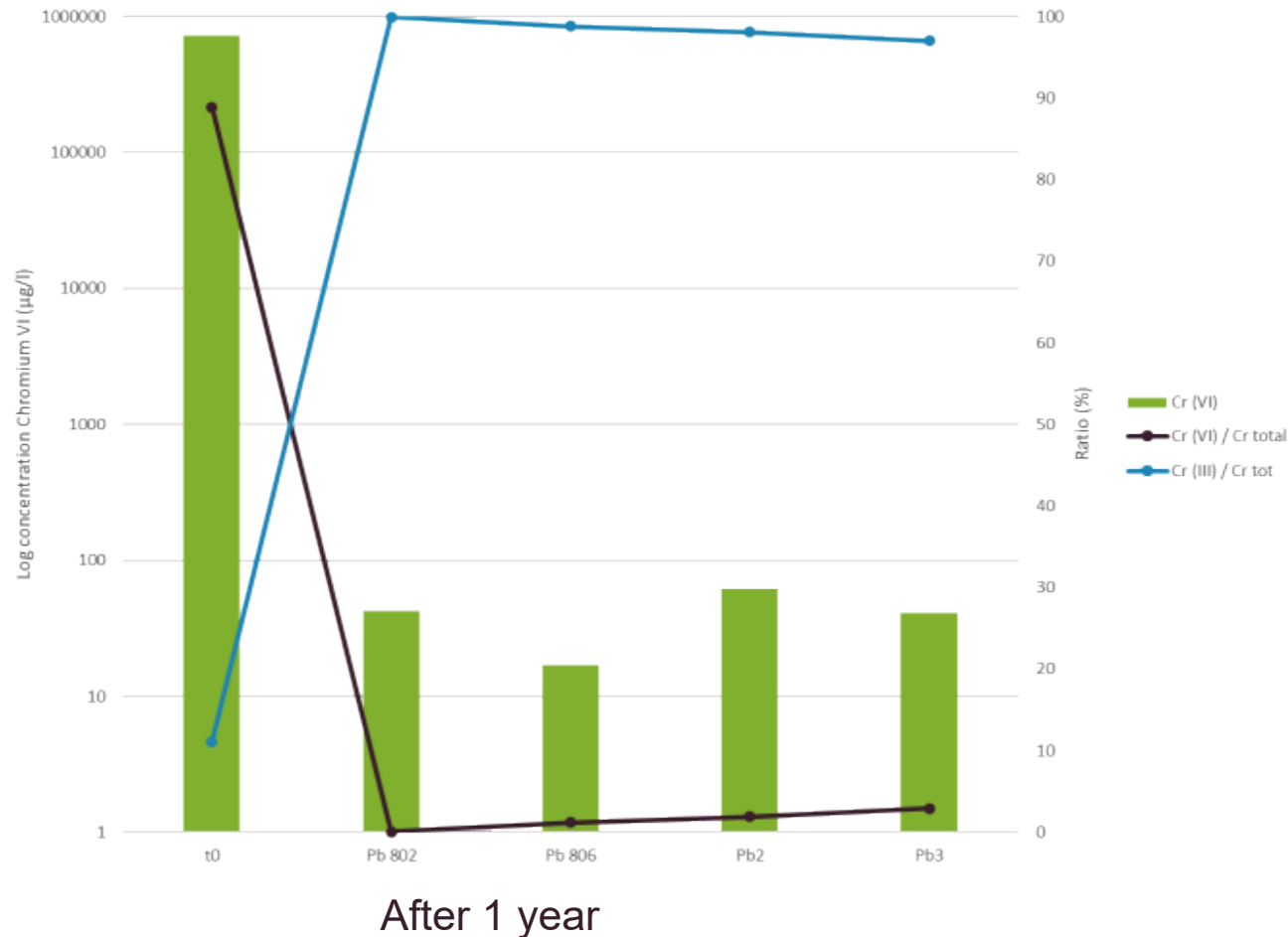
Cr (VI)	1,000,000 µg/l
TCE	100,000 µg/l
cDCE	53,000 µg/l
VC	3,600 µg/l
SO ₄ ²⁻	1,500 mg/l



Chromium (VI) in-situ remediation



Chromium (VI) in-situ remediation



- No limits for Cr defined: risk based
- Long term stability: followed up by monitoring (natural redox conditions are reducing)

Site

Vanadium (V) and sulphate contamination in the groundwater at a former mining and production site

- Former vanadium mine/production site. Currently intended for agricultural use.
- Concentrations: $\pm 1,000$ mg/L V(V), $\pm 5,000$ mg/L sulphate (leaching dump)
- Microbially mediated reduction of vanadium (V) to less mobile and toxic forms was investigated as a viable option.

1st laboratory test: results

- Vanadium reduction took place in the beginning of the test; no correlation with sulphate reduction
- Based on NGS, *P. putida* (obligate aerobic bacteria) possible candidate for vanadium reduction - 8 % of total bacteria + described in literature as being able to reduce Vanadium
- Starting material likely contained dissolved oxygen to some extent (presence of iron (hydr)oxides upon arrival)

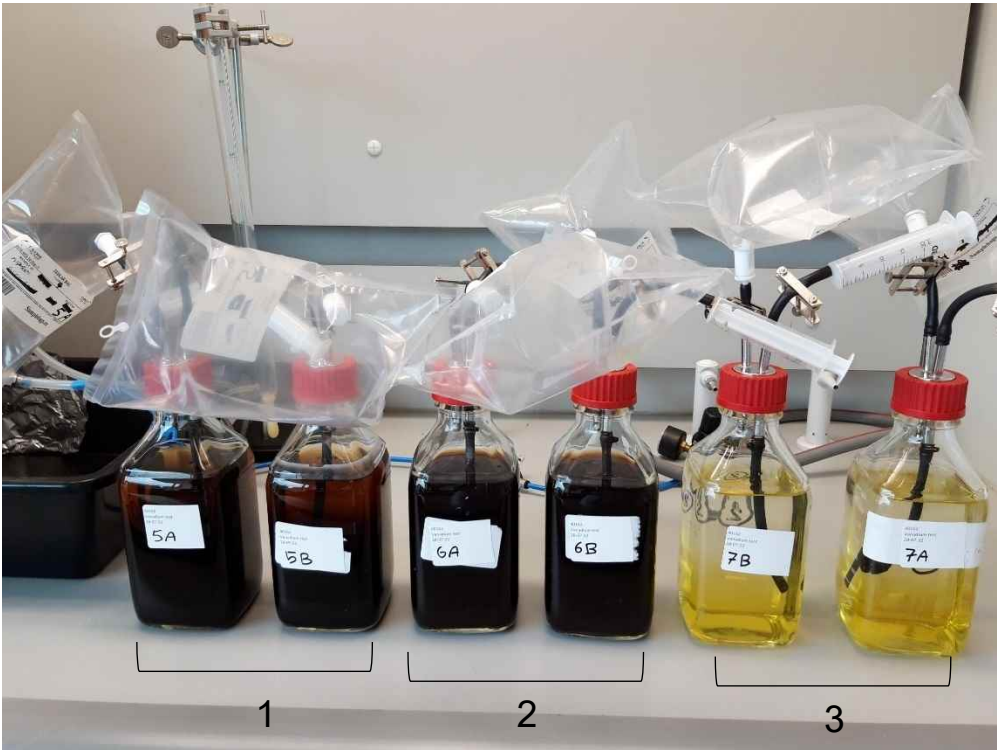
2nd Laboratory test: Aerobic and anaerobic

- Incubation under aerobic condition (+ growth substrate) to test if V reduction can take place under aerobic conditions **-> No reduction**
- Incubation under anaerobic conditions with strict anaerobic (new) material

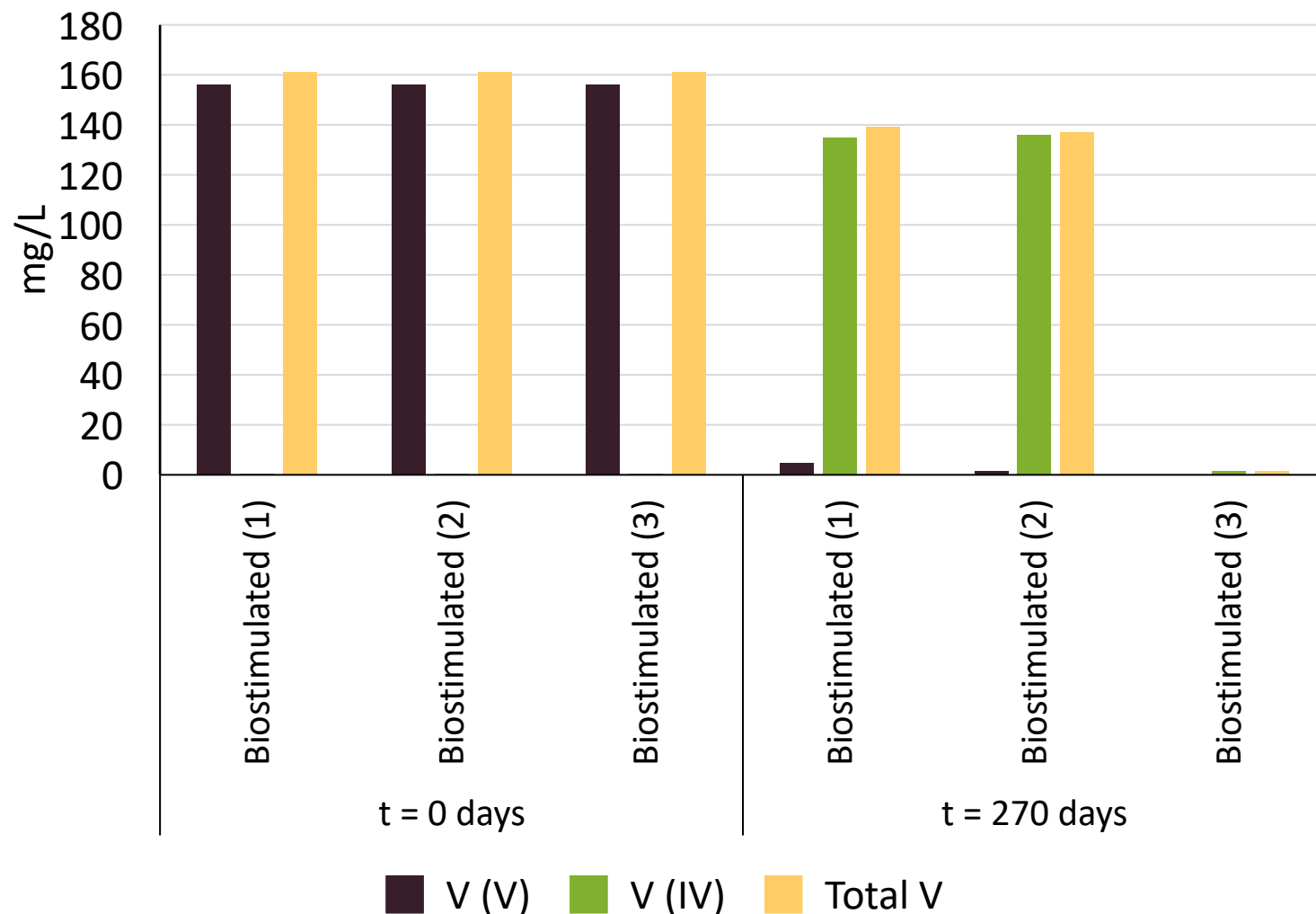
Anaerobic test: set up

- Complex organic substrate (Dehalo GS) and lactate as electron donors
- Iron sulphate might enhance sulfide and vanadium precipitation
- Lactate as substrate for better visible observations (colorless)

	Conditions	Amendments
1	Biostimulated 1	groundwater + electron donor Dehalo GS
2	Biostimulated 2	groundwater + electron donor + FeSO4
3	Biostimulated 3	groundwater + lactate + N/P



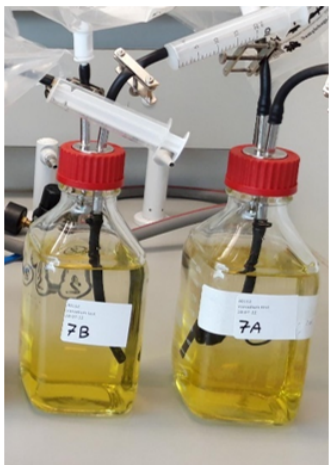
Anaerobic test: results



- 95-99% of total V was reduced
- >99% of total dissolved V was precipitated in lactate/phosphate condition

Anaerobic test: vanadium color changes

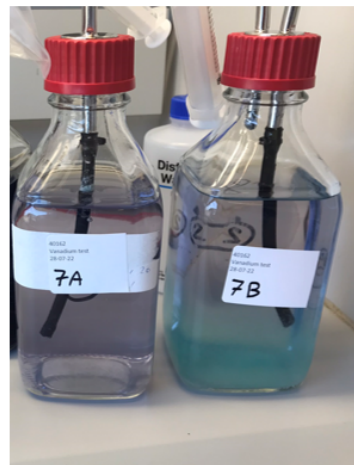
t = 0



7 days



26 days



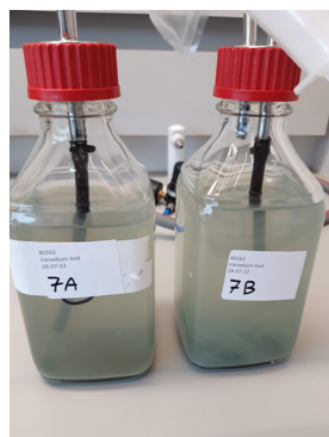
40 days



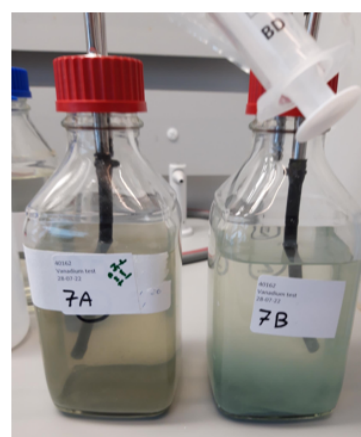
63 days



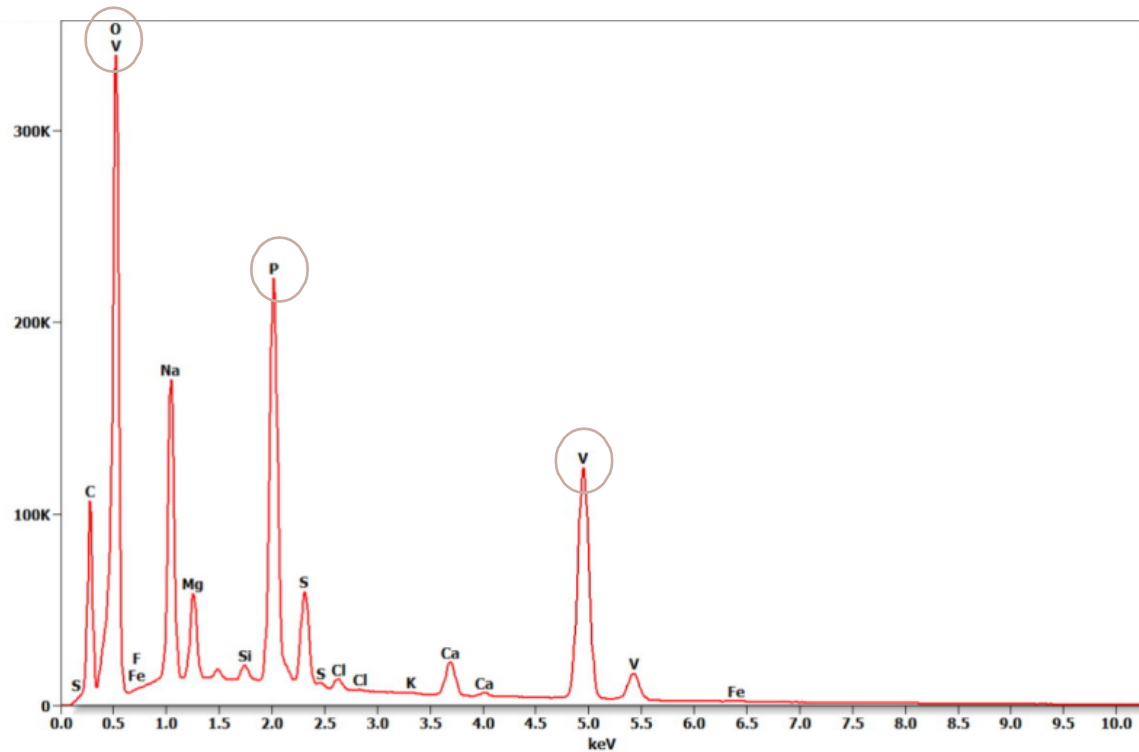
89 days



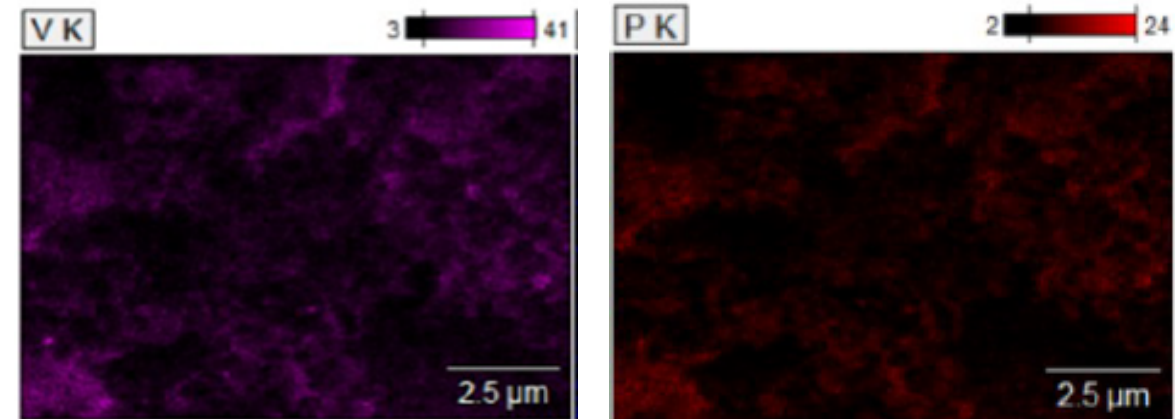
180 days



Anaerobic test: precipitation analyses

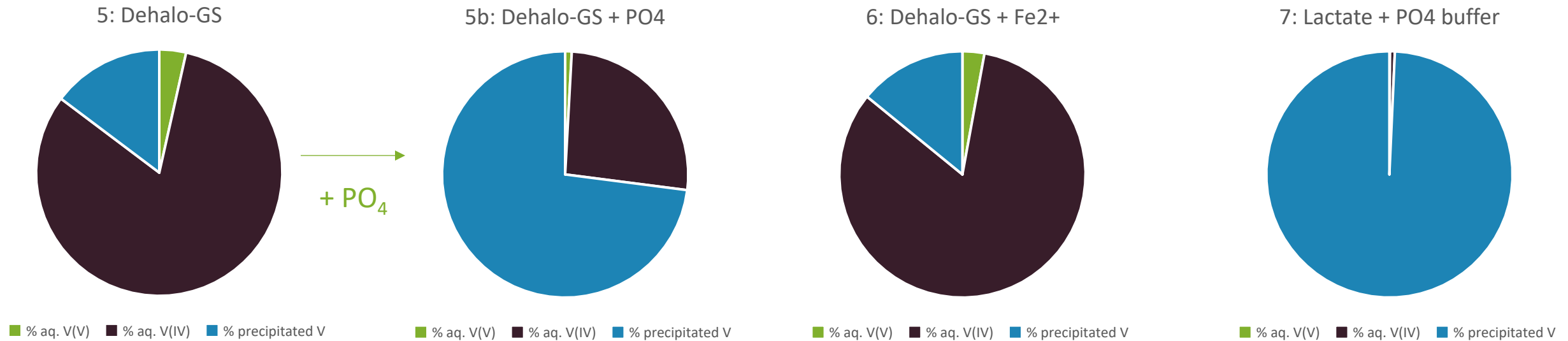


- Vanadium/phosphate complex?



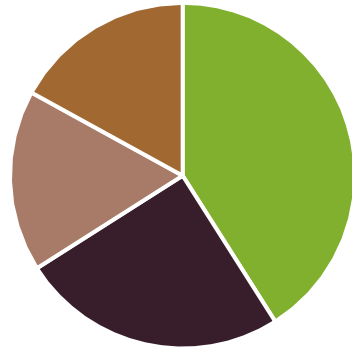
SEM-EDX

Anaerobic test: results



- >99% of total dissolved V was precipitated in lactate/phosphate condition

Anaerobic test: microbial analyses (NGS)



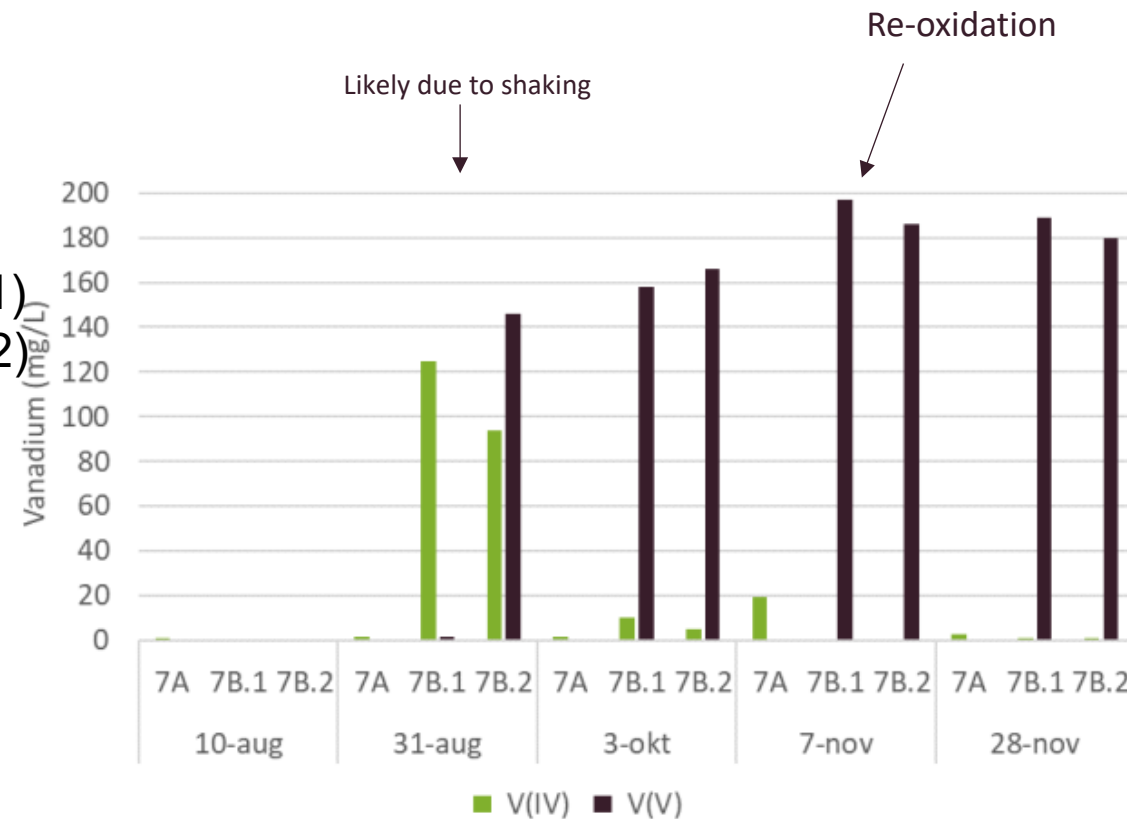
- potential Cr(VI) reducing bacterial species (*Pseudomonas stutzeri*)
- Sulphate reducing bacteria (variety of *Desulfosporosinus*)
- Fermenting bacteria (*Clostridia*)
- Other

- Different species than first test (also different material)
- Vanadium likely used as electron acceptor (literature: vanadate (VO_4^{3-}) as electron acceptor for *Pseudomonas aeruginosa* etc)

Long-term stabilization of reduced Vanadium

- Investigate stability of precipitated, reduced Vanadium under three conditions for 3 months

1. Anaerobic (7A)
2. Worst-case 1; headspace flushed once (7B.1)
3. Worst-case 2 headspace flushed weekly (7B.2)



Conclusions

- Up to 99% reduction of V(V) to V(IV) in the presence of growth substrate under anaerobic (likely nitrate reducing) conditions. Biological process!
- Up to 99% precipitation in the presence of sufficient phosphate
- Vanadium reduction reversible process. Quick re-oxidation in worst-case scenario, but no re-oxidation under anaerobic conditions
- Next steps: field conditions different than laboratory conditions (low DO, no shaking) -> test under field conditions

Thank you for your attention

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