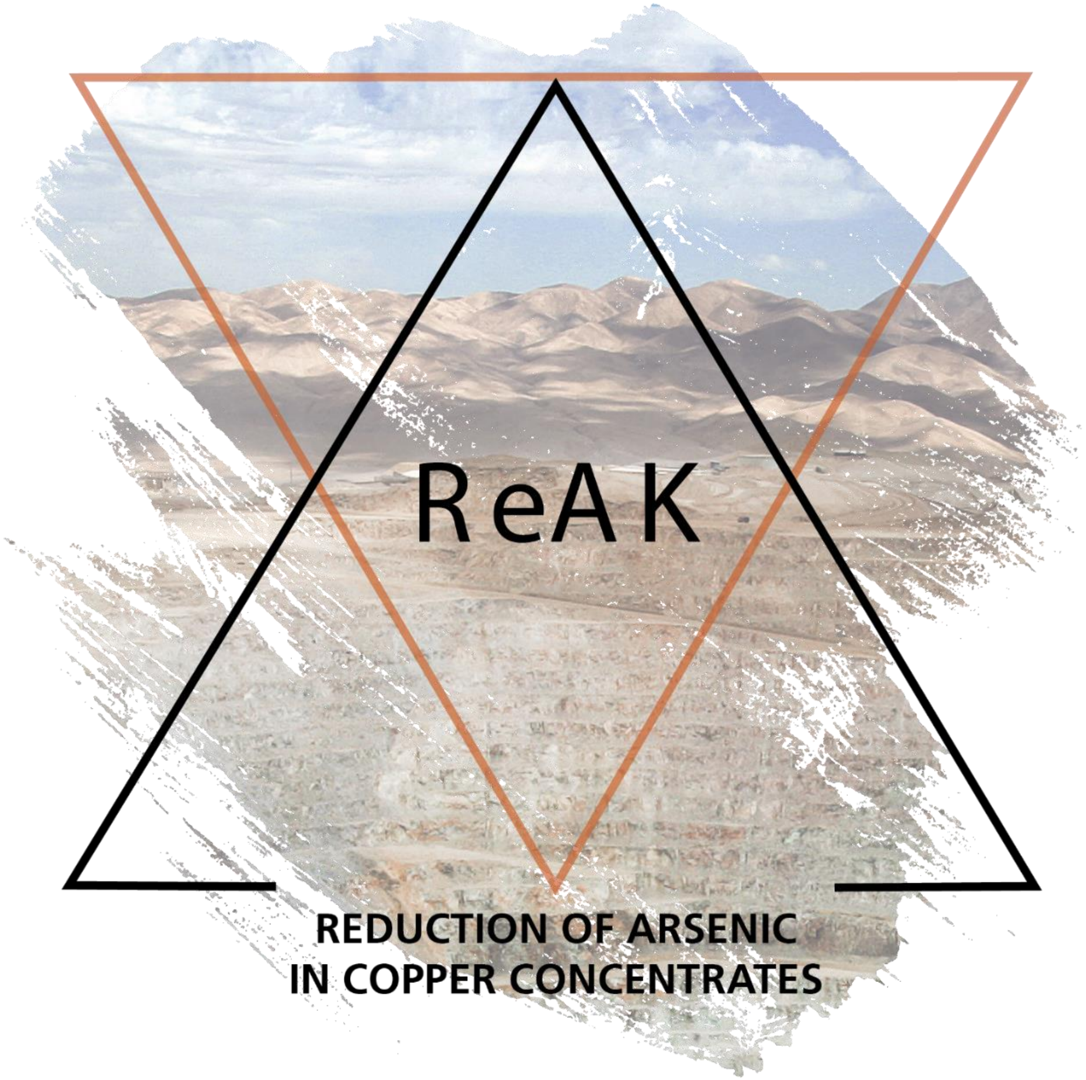
ReAK
REDUCTION OF ARSENIC
IN COPPER CONCENTRATES



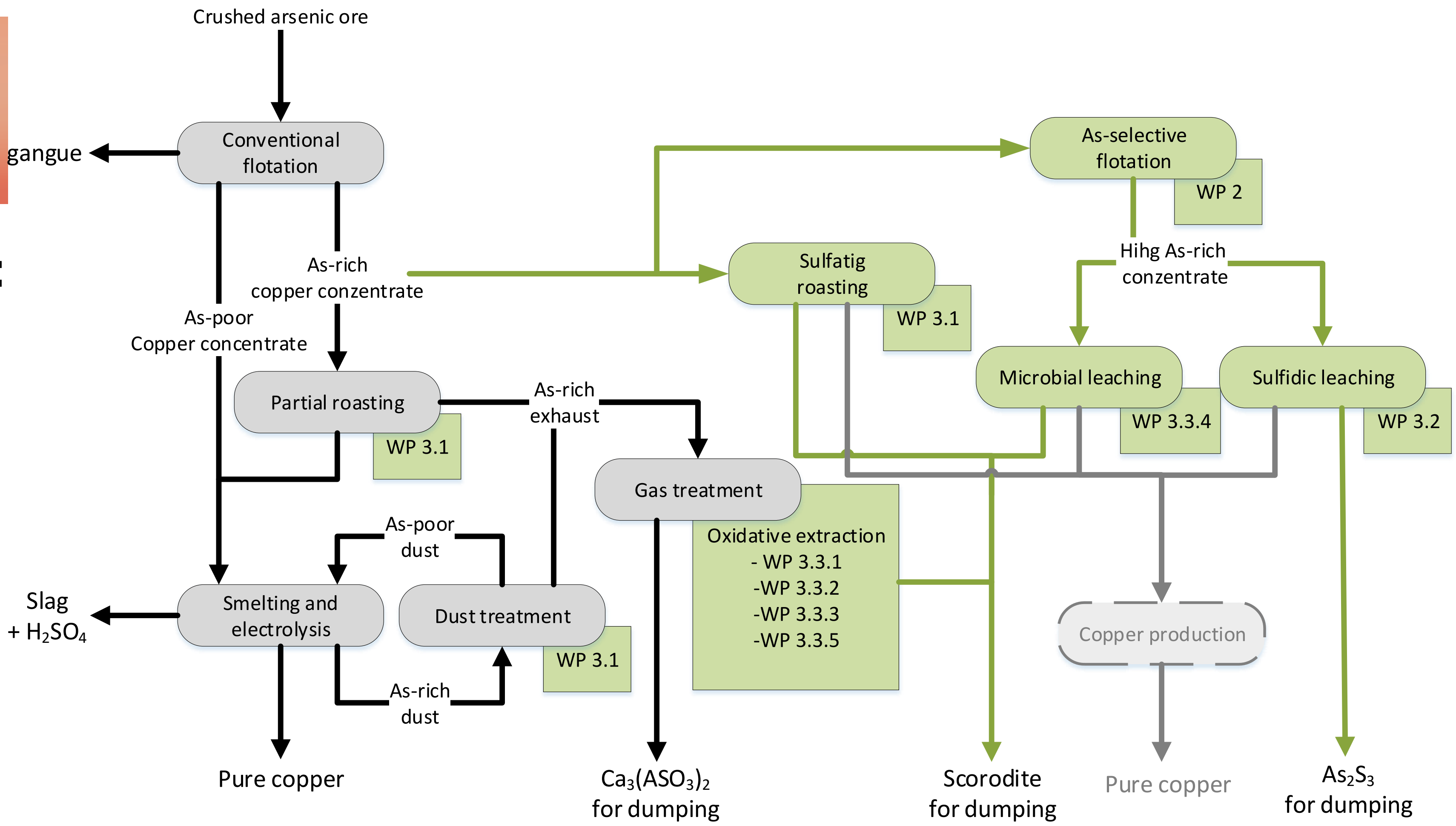
The ReAK Project

with a focus on oxidation and mobilization of arsenic from the mining industry
April, 08th 2022,

ReAK

Project information:

- Funding authority:
  Client II-program
  of the Federal Ministry
  of Education and Research
- Duration:
  01.09.2019 – 31.08.2022
- Volume: 3.6 million €
  (2.85 million € funding)



- Target
  Optimization and further development of existing processes and establishment of new processes for the treatment of arsenic-rich copper ores and their concentrates.

ReAK

Aurubis
BGR
Borregaard
EKOF Mining & Water Solution GmbH
Innovation für Wassertechnik ENVIROCHEMIE
Fraunhofer IWKS
Metso:Outotec
TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.
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WP 0 Project management and coordination (**IWKS**)

Pretreatment and concentration of arsenic

Stabilization of arsenic

Strategy and concept

WP 1 Systematic characterization of the starting material (**BGR**) — CODELCO

WP 2 Selective flotation (**EKOF**)

WP 3 Treatment of arsenic-rich copper concentrates and dusts (**Outotec**)

- **WP 3.1** Roasting (**Outotec**) — Universidad de Concepción
- **WP 3.2** Sulphic leaching (**TUBAF**) — ecometales LIMITED, FILIAL CODELCO
- **WP 3.3** Oxidative extraction (**EC**) — ecometales LIMITED, FILIAL CODELCO

WP 4 Investigation of immobilisation and mobilisation processes of arsenic (**Wismut**) — ecometales LIMITED, FILIAL CODELCO; CODELCO

WP 5 disposal concept (**IWKS**) — ecometales LIMITED, FILIAL CODELCO; CODELCO

WP 6 LCA / LCC (**IWKS**) — ecometales LIMITED, FILIAL CODELCO

WP 7 Exploitation and dissemination of results (**IWKS**) — ALTALEY; AHK

Oxidation with UV/H_2O_2, Ozone, other alternatives?

- Development and testing of a simple method for As (As(III)/As(V)) analysis in aquatic solutions
- Oxidation tests with:
  - UV/H_2O_2 (incl. additives)
  - Ozone (incl. additives)
  - Alternative Oxidation (UV-B Light and oxidants)

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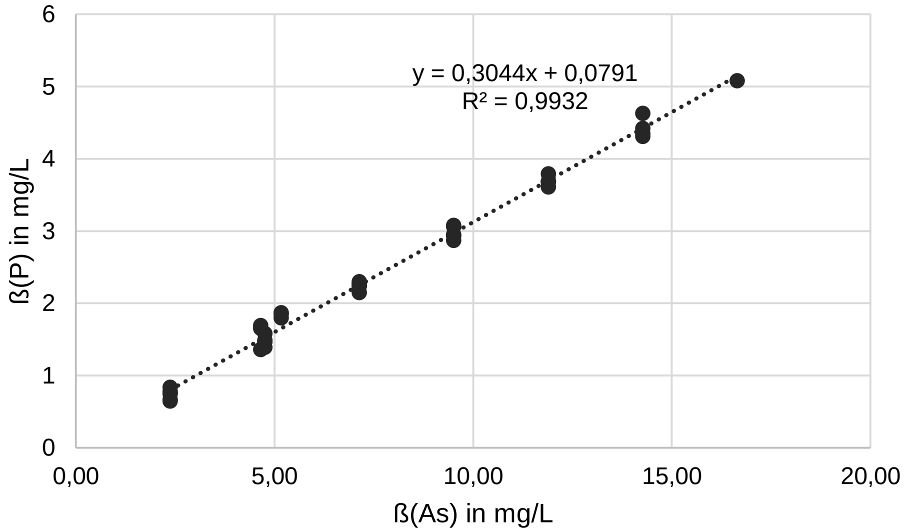
Analysis method As(III) / As(V) - “quick and easy”

- rapid determination of As(III) or As(V) by means of photometric rapid tests
- Use of the phosphate rapid test from water analysis (Ortho-phosphate for As(V); Total phosphate for As(III) and As(V))
- Interfering substances examined and characterized (on the basis of the possible wastewater matrix and reagents used (H_2O_2/buffer etc.))
- Recovery rate of 80 - 90%



Calibration line with one of the photometric quick tests

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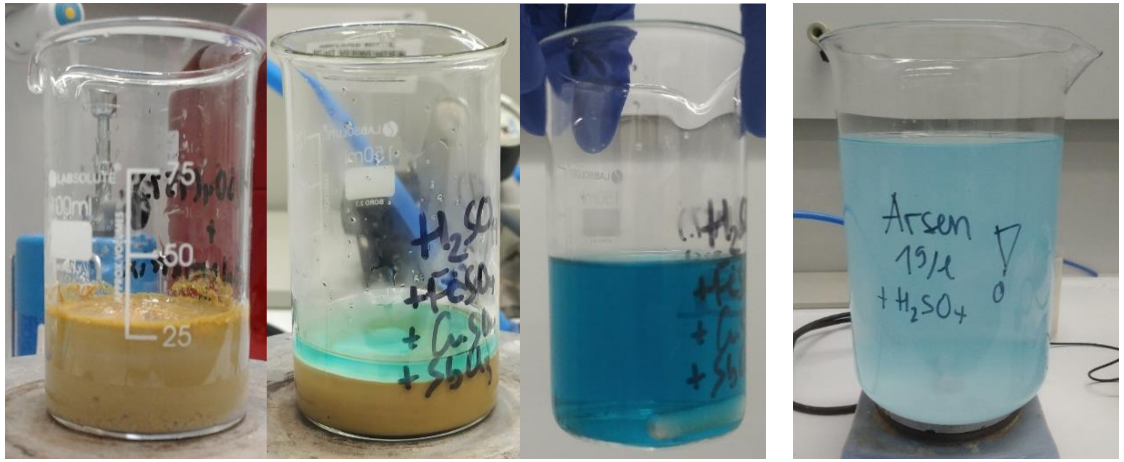
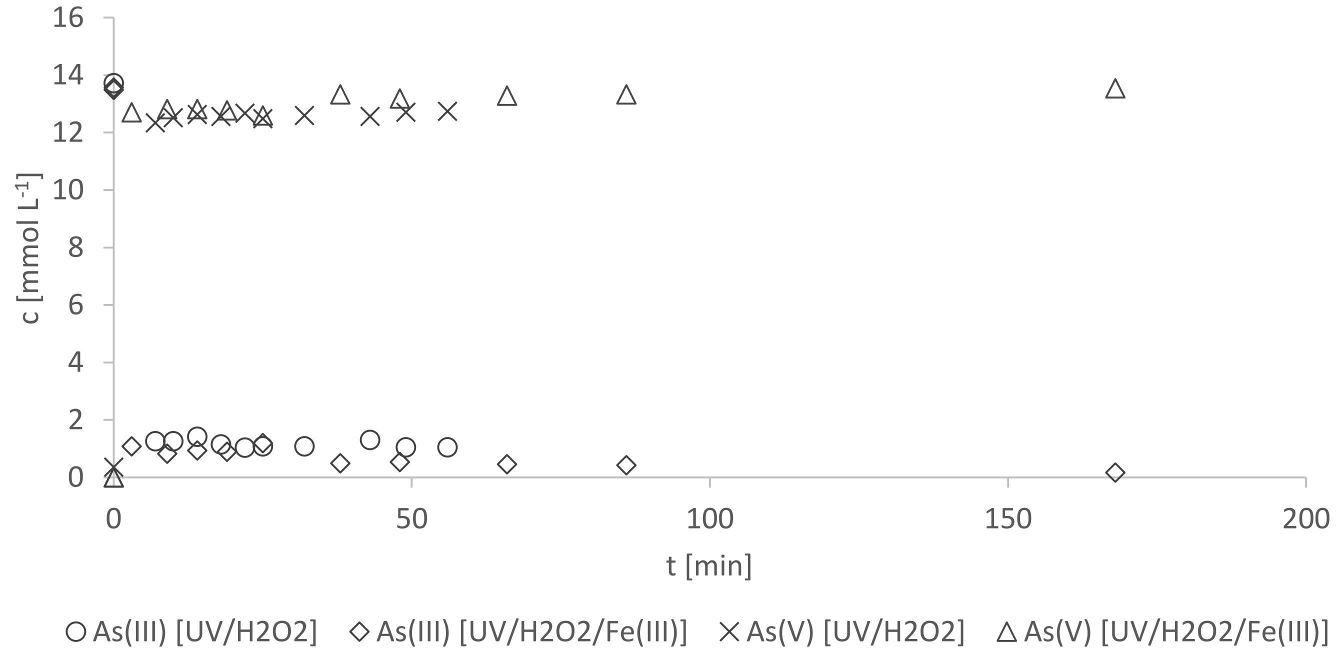
Oxidation Tests – general

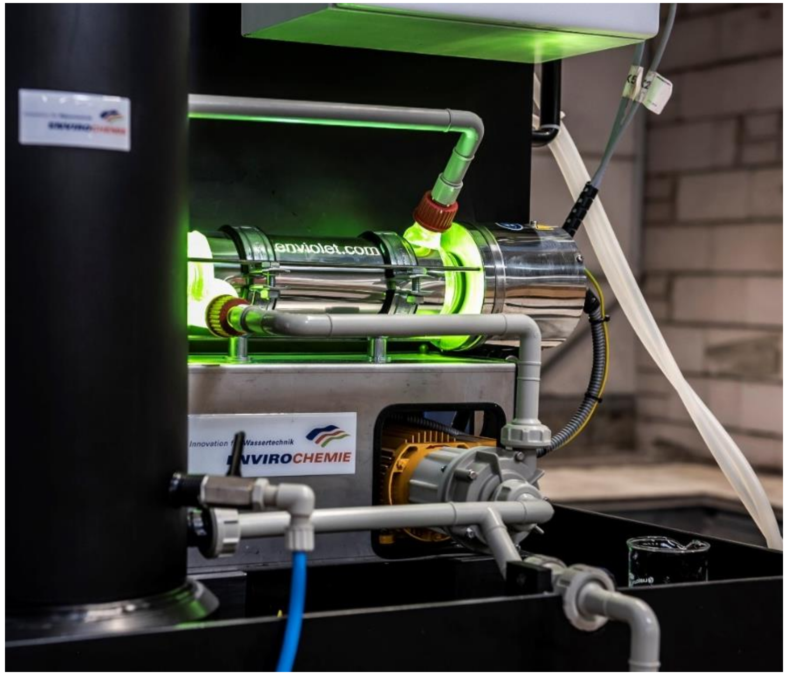
- Waste water matrix synthetically mixed together (based on available data)
- Varying the As concentration (0,5 – 5 g_{As}/l), other ingredients according to the concentrations listed below.



	H_2SO_4	As^{3+}	Fe^{2+}	Cu^{2+}	Sb^{3+}	Bi^{3+}	Cl^-	F^-
[g L^{-1}]	31,20	1,00	0,10	0,70	0,28	0,15	0,47	0,13
[mol L^{-1}]	0,3181	0,0133	0,0018	0,0110	0,0023	0,0007	0,0133	0,0068
Salt		**As_2O_3**	**$FeSO_4 \cdot 7H_2O$**	**$CuSO_4$**	**$SbCl_3$**	**$BiCl_3$**	**NaCl**	**NaF**
[g L^{-1}]		1,32	0,50	1,76	0,52	0,23	0,77	0,29

Oxidation Tests – UV/H_2O_2





- Single addition of 16.7 mmol L^{-1} H_2O_2
- Fast oxidation, As(III) degradation > 90%
- UV/H_2O_2/Fe(III) with better result (advantageous, as iron is present in the wastewater matrix
  → favours UV oxidation (Photo-Fenton))

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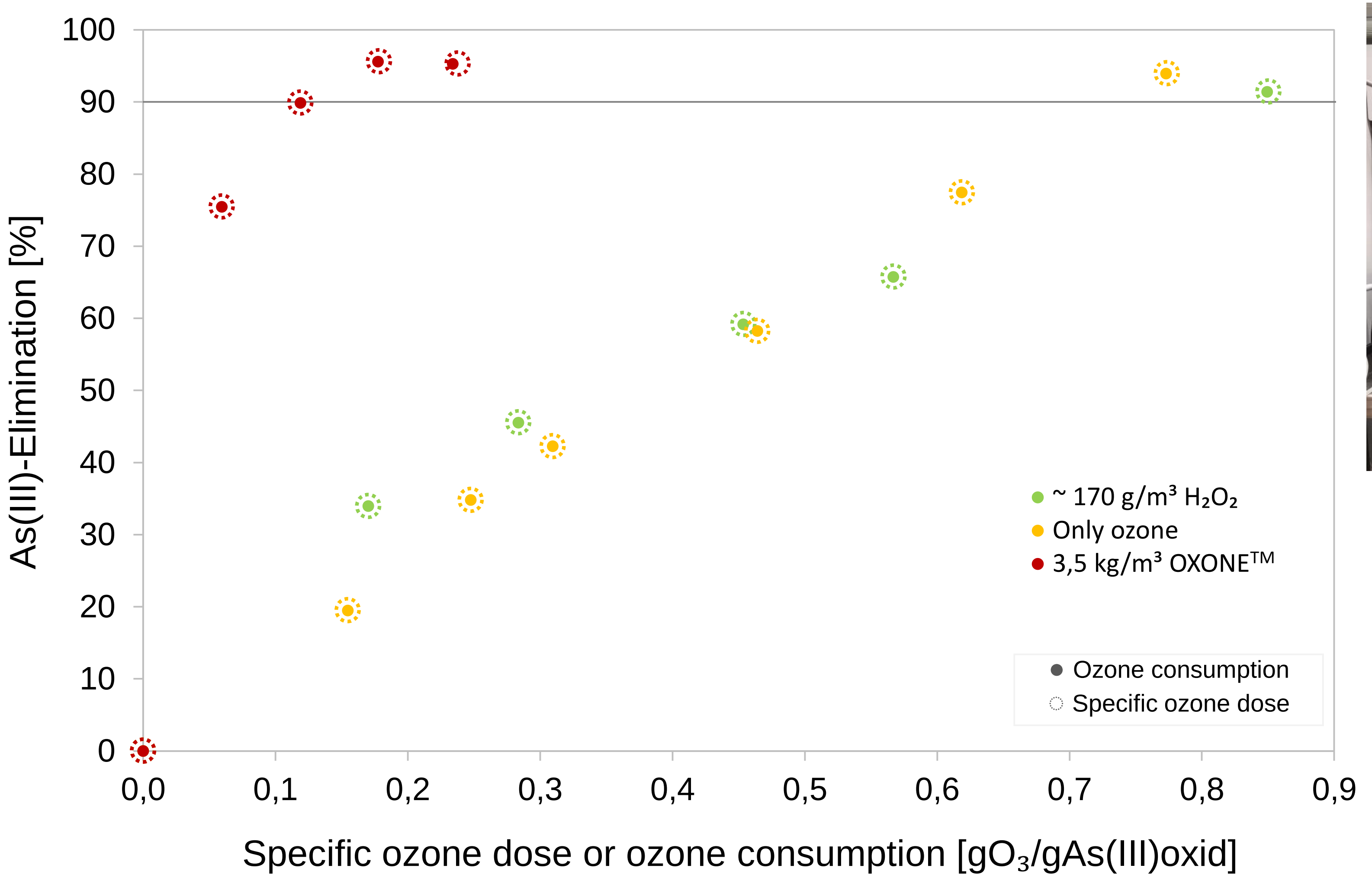
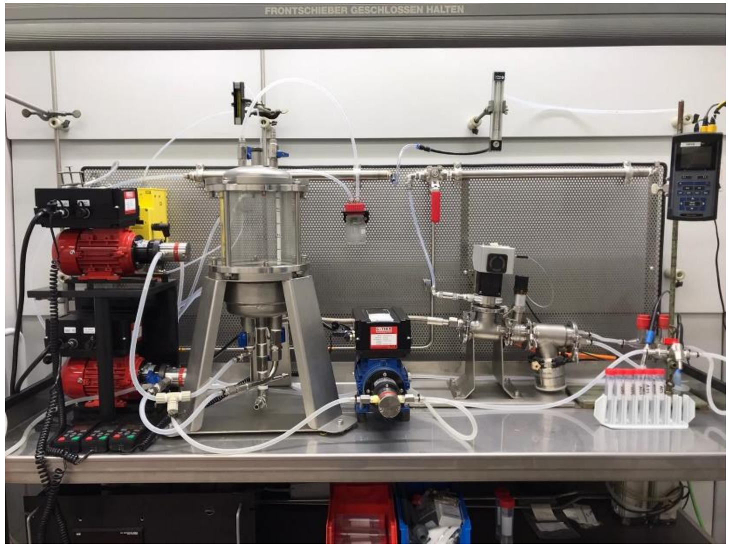
Oxidation Tests – Ozone (incl. Additives)





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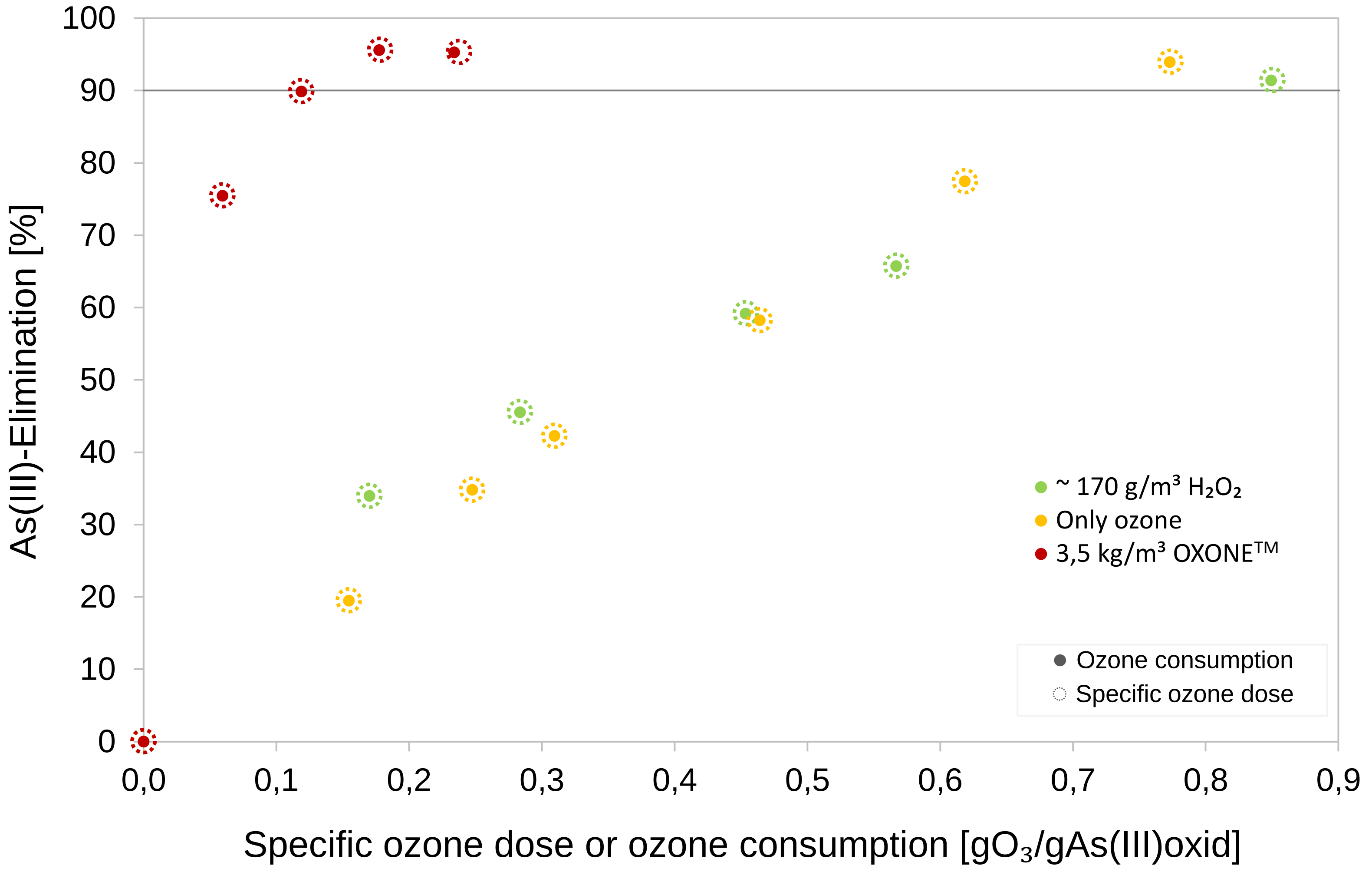
Oxidation Tests – Ozone (incl. Additives)



- Arsenite oxidation with ozone at a dose of approx. 0.7 g O_3/g As(III) at > 90%.
- Combination of Ozone + "Oxone" (potassium peroxomonosulfate (PMS)) delivered best results
- Tested amount of H_2O_2 as additive delivered no special benefit (higher dosage necessary)

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Alternative oxidation… why ?

- Ozone or UV/H_2O_2 oxidation works – Data collected on doses for 99% As-oxidation
- Consideration of feasibility and CAPEX/OPEX
- Sensitive technologies for a harsh environment
  - UV-Lamps are sensitive against particles and turbidity of the waste water
  - Ozone production requires a lot of oxygen (10 times the amount of ozone needed) and the entire process requires enormous cooling capacities (e.g. ozone generator).
- *What price are we competing against ?*
- Taking advantage of given situations - lots of sun ... much UV-B radiation

Alternative oxidation... Idea !

- Oxidation through sunlight (esp. UV-B & UV-A radiation)
- Reactor with coating of titanium dioxide TiO_2 (catalyst)
- UV-Lamp that imitates sunlight of the desert (for the lab tests)
- Idea: Water flows very slowly over the surface
- Arsenic is oxidized by OH- or SO_4-Radicals produced by catalyst and radiation

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Oxidation with UV/H_2O_2, Ozone, other alternatives? Conclusion

- Tested different oxidants
  - O_3
  - UV/H_2O_2
  - Sulfate radical oxidation (PMS/PDS)
  - Alternative Oxidation (UV-B and oxidants)
- all oxidants investigated show an effect in the wastewater matrix (oxidation of As(III) to As(V)) – only a matter of the dose
- now a technology has to be simulated which performs best under the given circumstances (desert, infrastructure etc.) and economic factors

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Oxidation with UV/H_2O_2, Ozone, other alternatives? Outlook

- Actual situation at the mines ?
- Doses of oxidants (mostly H_2O_2) ?
- What are we competing against ?

- When this data is transferred, we can compare a large-scale installation of the alternative processes to the current situation.

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Electrochemical oxidation
Test setup

Laboratory experiment:

Volume	200 ml
Electrode area	40 cm² (2* 20cm²)
Amperage	2 A
Time	80 min
Concentration (As)	17,5 g/L As^{3+} from As_2O_3
Concentration (Fe)	90 mg/L
Concentration (Cu)	700 mg/L

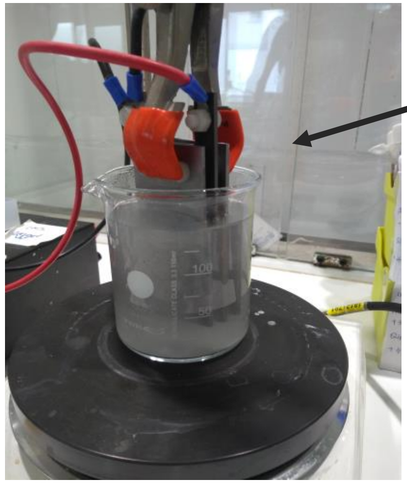
Cathode reaction:

$$2\,H^+ + 2\,e^- \rightarrow H_2 \uparrow$$

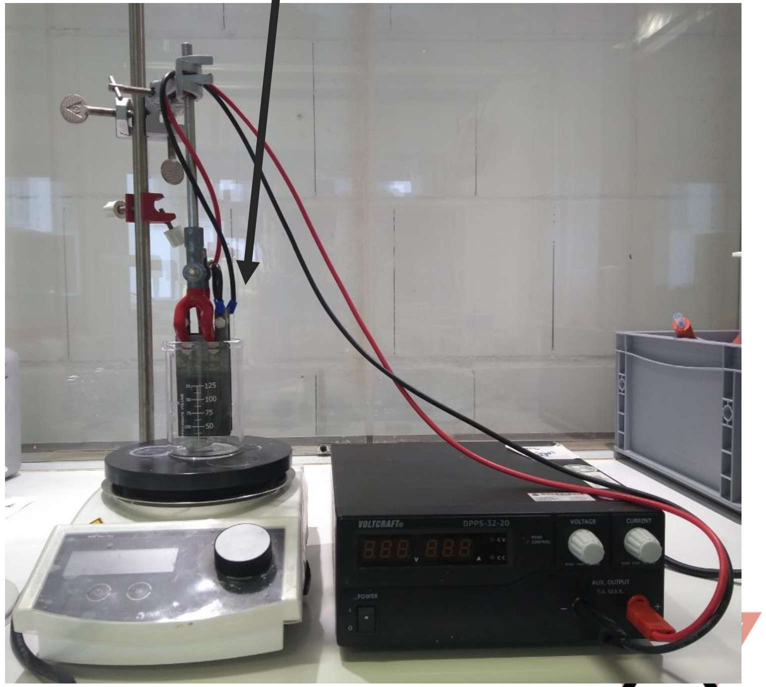
Anode reaction:

$$As^{3+} \rightarrow As^{5+} + 2\,e^-$$

→ Oxidation seems to occur indirectly via hydroxyl radicals

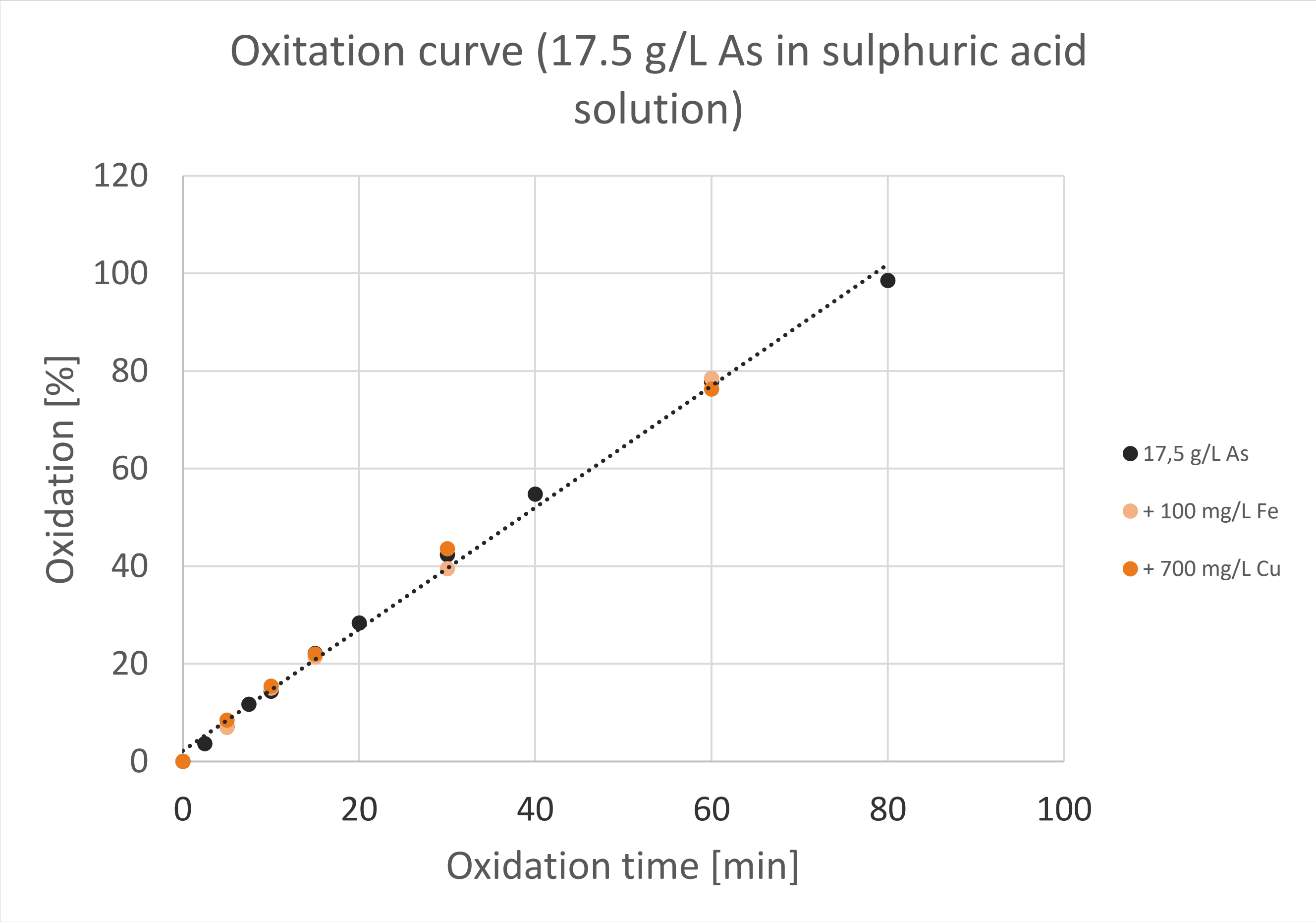


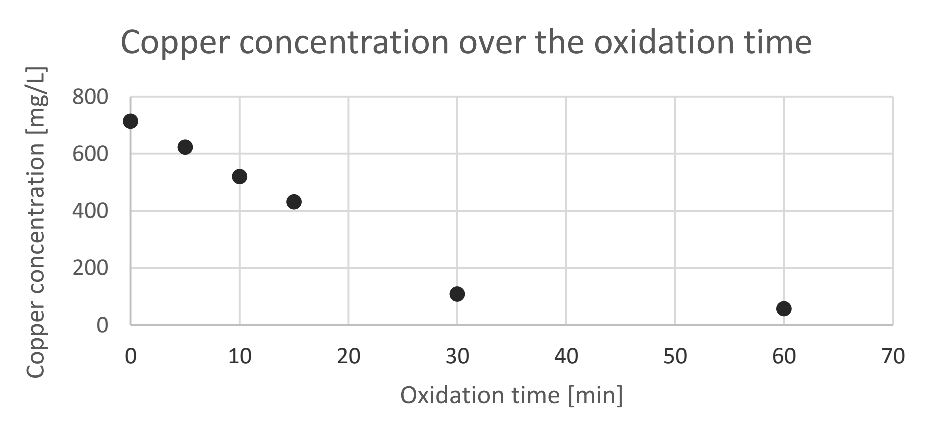
Diamond electrode
surrounded by two steel electrodes as cathodes

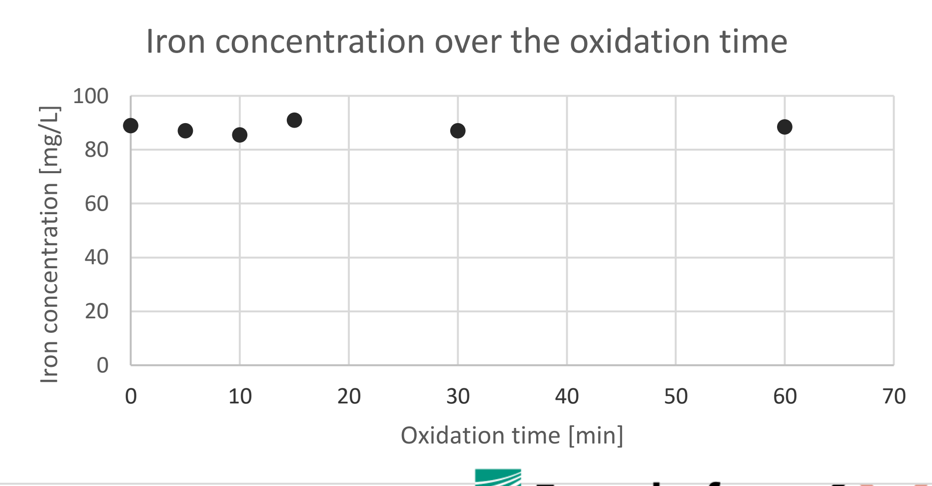


Fraunhofer IWKS

Lab experiment







Fraunhofer IWKS

First approximations based on Faraday's law:

Real conditions:

Volume	1920 m³/d
As^{3+}-Concentration	18,2 g/L

Calculations from the laboratory results:

Volume	200 ml	**110667 L**
Conc. (As)	17,5 g/L	**18,2 g/L**
Electrode area	40 cm²	**2213 m²**
Current	2 A	**1106,5 kA**
Electrolysis time	80 min	**83 min**

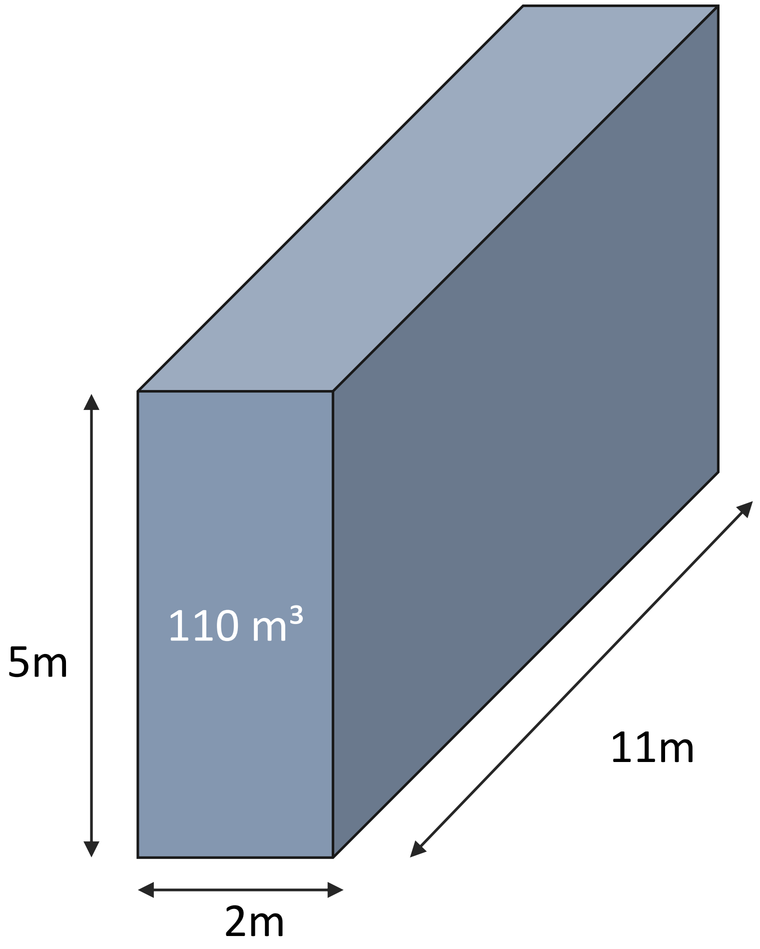
Faraday Law:

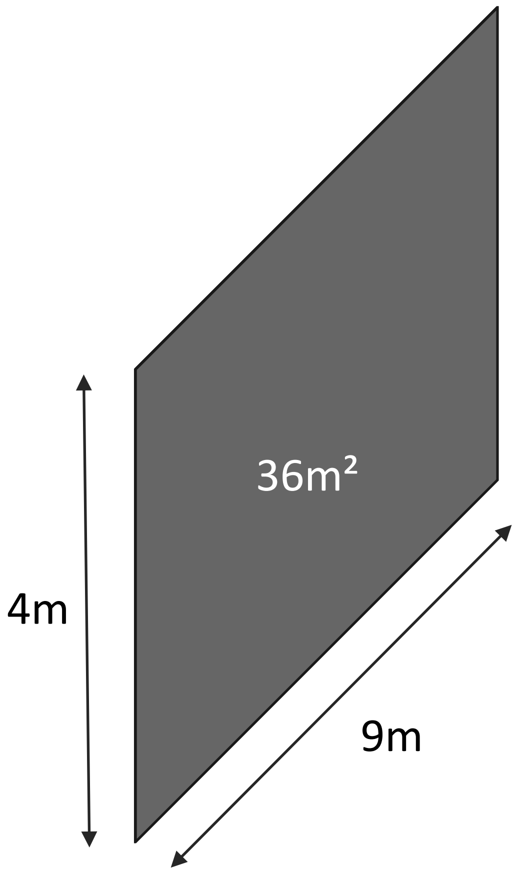
$$n = \frac{m}{M} = \frac{I * t}{z * F}$$

n = amount of substance [mol].
m = mass [g]
M = molar mass [g/mol]
I = Current [A]
t = time [s]
F = Faraday constant
= 96485.3 As/mol
z = valency

Fraunhofer
IWKS

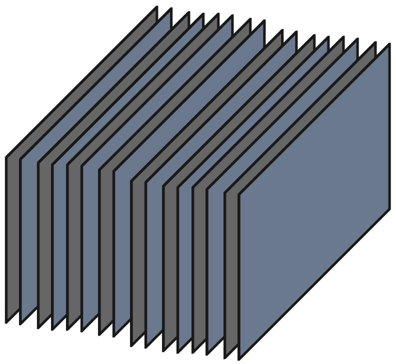
How could this look like …





coated on both sides

Diamond electrode and steel electrode alternately

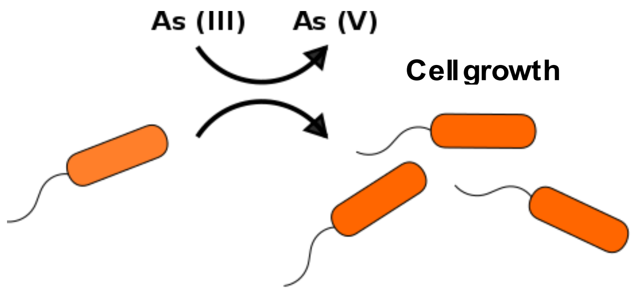


$36m^2 * 2 * 31 = 2232m^2$

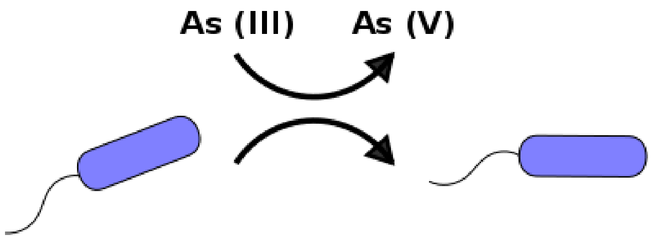
Fraunhofer IWKS

Microbiological arsenite (As(III)) oxidation

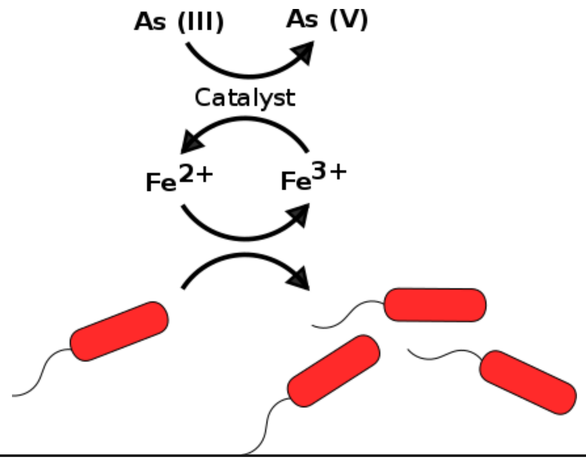
Lithoautotrophic arsenite oxidation



Heterotrophic bacterial arsenite oxidation



Indirect arsenite oxidation



Arsenite oxidation in acidophiles (biomining microorganism)

- Search for new ways to oxidize arsenite!
- There has not been a lithoautotrophic arsenite oxidizing acidophile bacteria described

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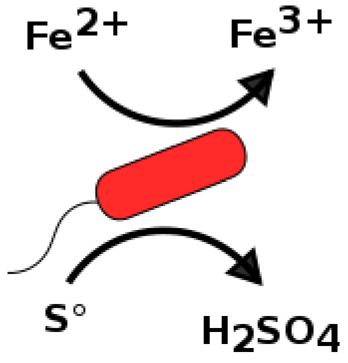
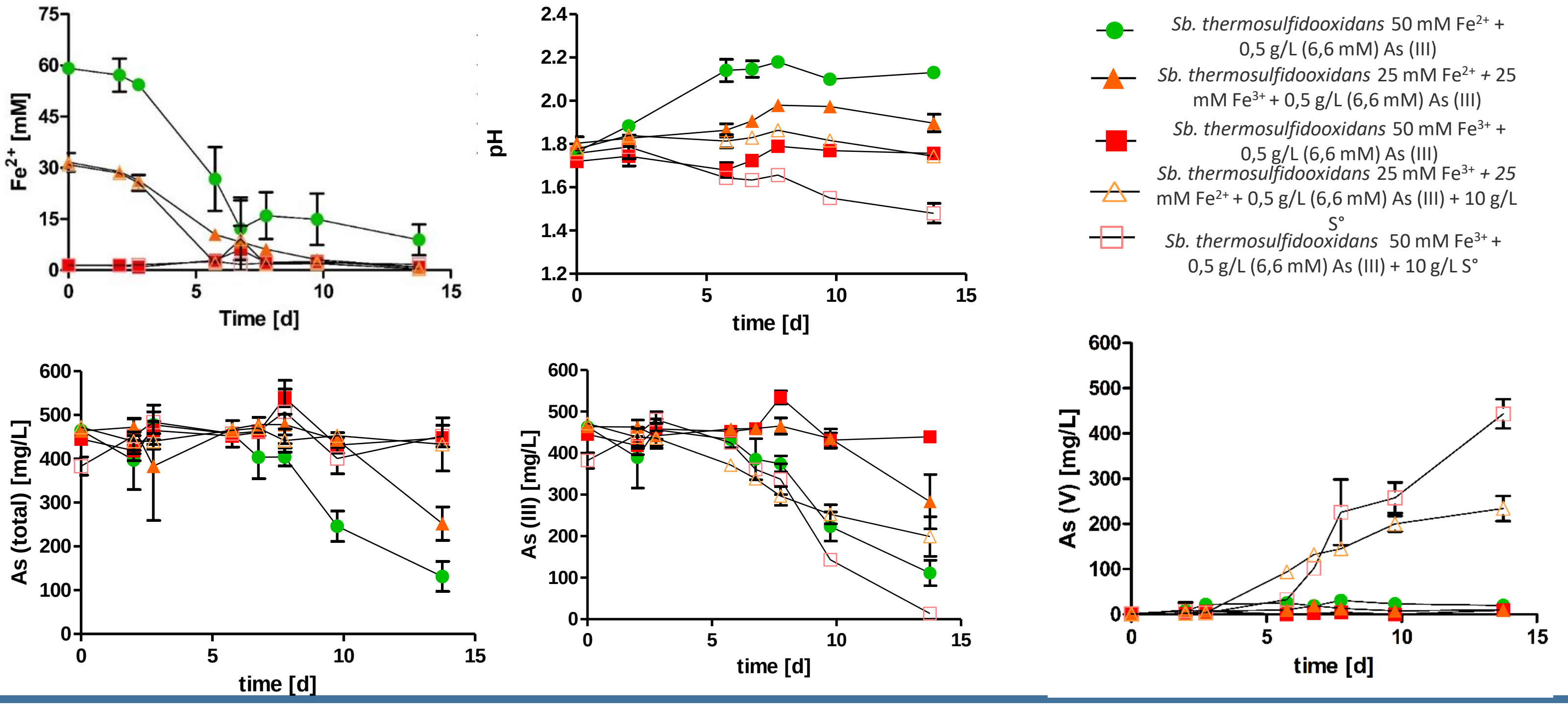
Sulfobacillus thermosulfidooxidans indirect arsenite oxidation.



Sb. Thermosulfidooxidans As (III) oxidation in presence of Fe^{3+} and S °.



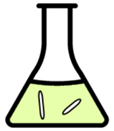
Sb. thermosulfidooxidans is able to indirectly oxidize As (III) by oxidizing S° in presence of Fe^{3+}.

Isolation of a new litoauthotropic arsenite oxidizing acidophile strain

Reiche Zeche (Freiberg)

Sample extraction

3 times Enriched

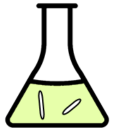


By using As (III) in mac medium at acid ph (1,8)

Plated 2 times

By using As (III) in mac medium at acid ph (1,8)

Isolation



By using As (III) in mac medium at acid ph (1,8)

Characterization of the new strain:

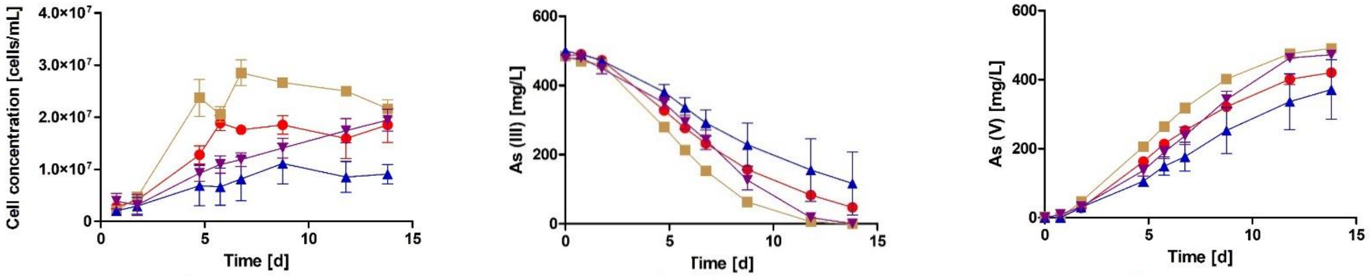
16S DNA sequecing

Ac. acidophilum CJR1

Genome sequencing in progress

Characterize its growth and As (III) oxidation activity

Cell growth and As (III) oxidation of *Ac. acidophilum* CJR1 using 0,5 g/L As (III) at different pH in Mac medium.



Ac. acidophilum CJR1 0,5 g/L As (III) pH 1,8

Ac. acidophilum CJR1 0,5 g/L As (III) pH 2

Ac. acidophilum CJR1 0,5 g/L As (III) pH 2,5

Ac. acidophilum CJR1 0,5 g/L As (III) pH 3

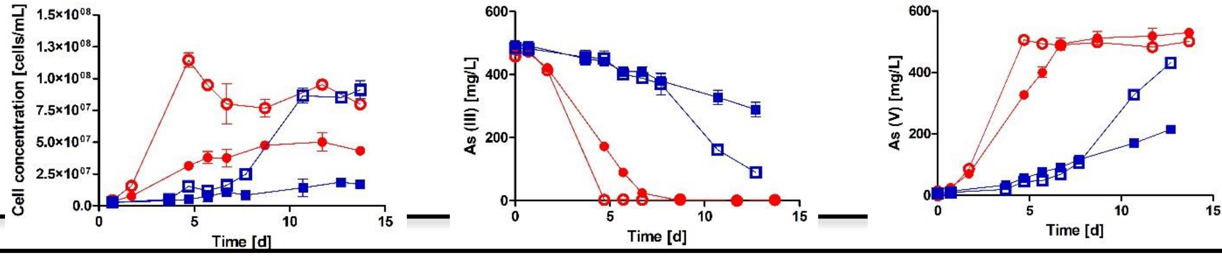
Cell growth and As (III) oxidation of *Ac. acidophilum* CJR1 using 0,5 g/L As (III) with or without Yeast Extract (YE) 0,2 g/L at different pH in Mac medium.

Ac. acidophilum CJR1 0,5 g/L As (III) pH 2

Ac. acidophilum CJR1 0,5 g/L As (III) + YE 0,2 g/L pH 2

Ac. acidophilum CJR1 0,5 g/L As (III) pH 1,5

Ac. acidophilum CJR1 0,5 g/L As (III) + YE 0,2 g/L pH 1,5



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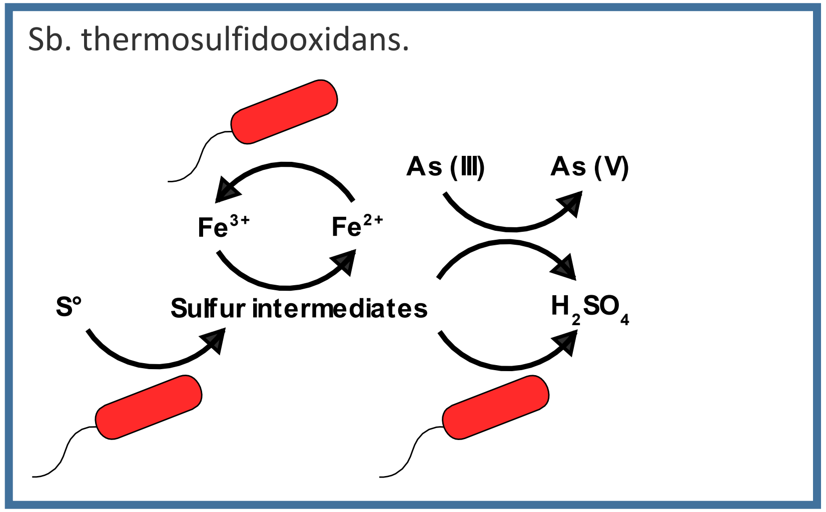
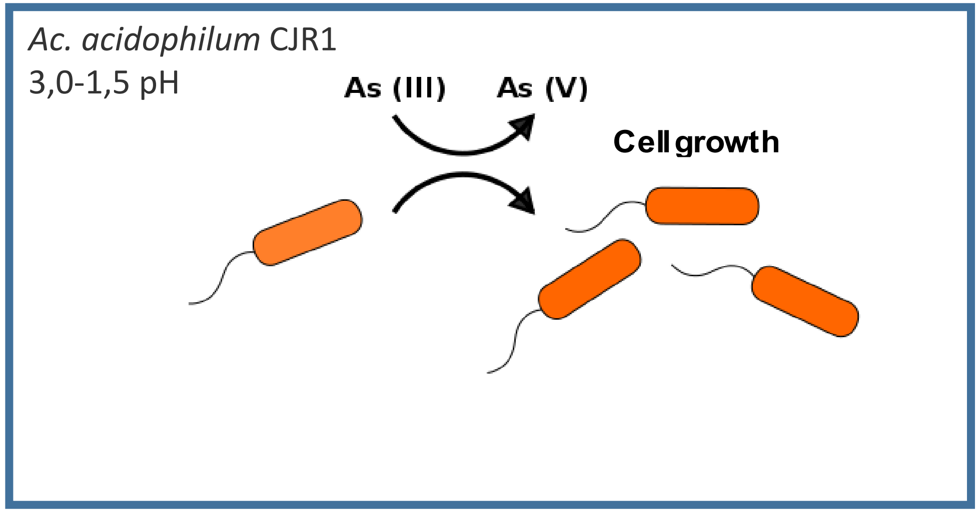
Microbiological oxidation - Conclusion

- We documented *Sb. thermosulfidooxidans*'s indirect As (III) oxidation by an unknown mechanism, that needs the presence of Fe^{3+} and the oxidation of S °. We propose an explanation in the image.
- We found a new chemolithotroph As (III) oxidizing strain of *Ac. acidophilum*. The new strain received the name of *Ac. acidophilum* CJR1.





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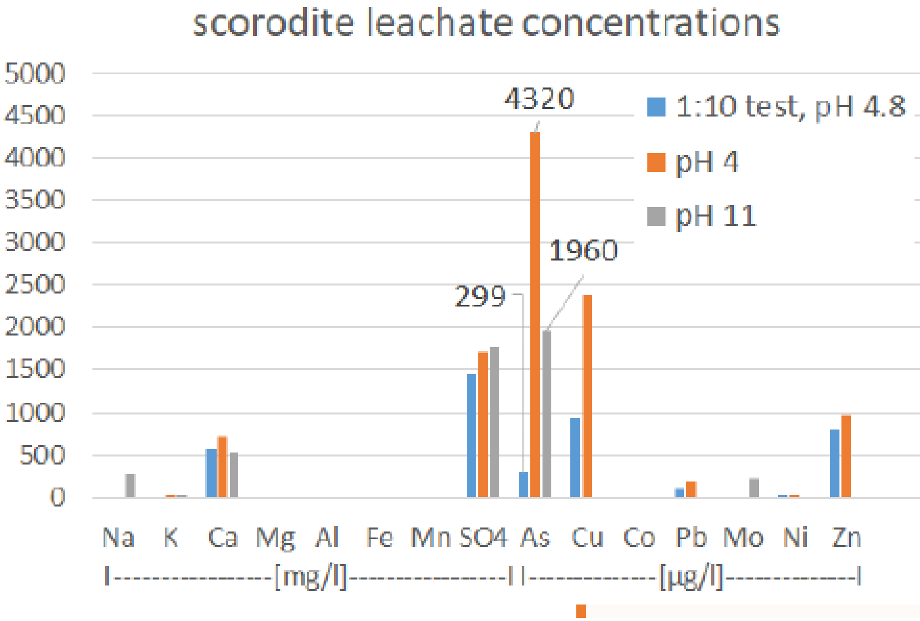
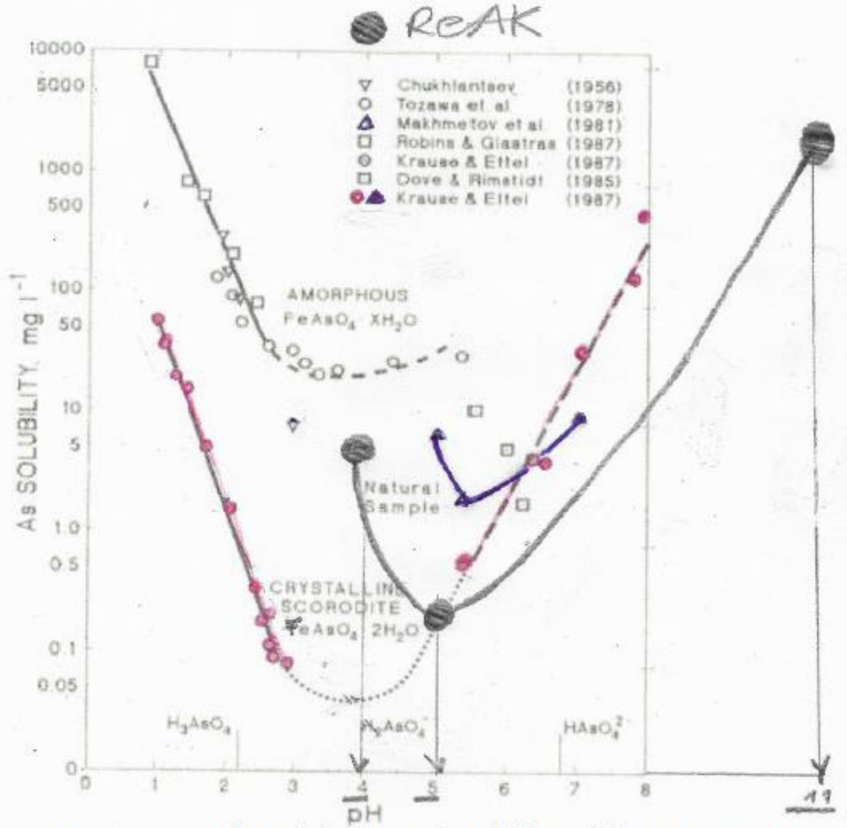
Immobilization and mobilization reactions of As – classification tests (Scorodite Ecometales Calama)



- pH 4 (24 h): 0.5 M HNO_3, 1.8 mmol/kg
- pH 11 (24 h): 1 M NaOH, 125 mmol/kg
- Repeat pH 4 Test



Krause, Ettel: Solubility and stablility of ferric arsenate compounds, Hydrometallurgy 22(3), 1989

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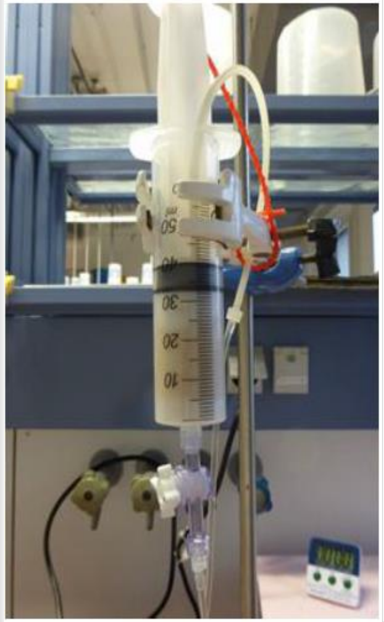
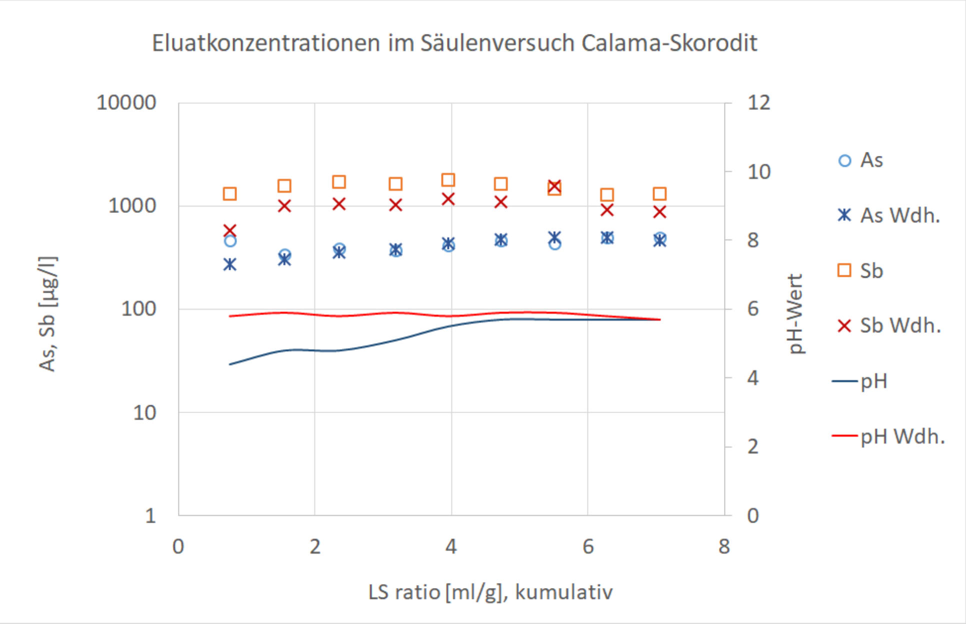
Leaching tests at simulated field conditions





Test	pH-value	As-Concentration, mg/l
pH-stat. pH=4	4	4,3
S4	4,8	0,3
Säulenelution	5,85	0,5
pH-stat. pH=11	11	2,0

- 20 g of Calama Scorodite (1mm < d < 2mm) with 15 ml Aqua dest.
- Discontinous treatment with Aqua dest. (3 h/d with Flowrate Q=5mL/h over 9 d)
- Daily change of the bed volume (Q = 15 mL/d)
- Equilibrium pH value at 5.8-5.9
- Further experiments with different pH (4.5-8), different water load and temperatures are planned

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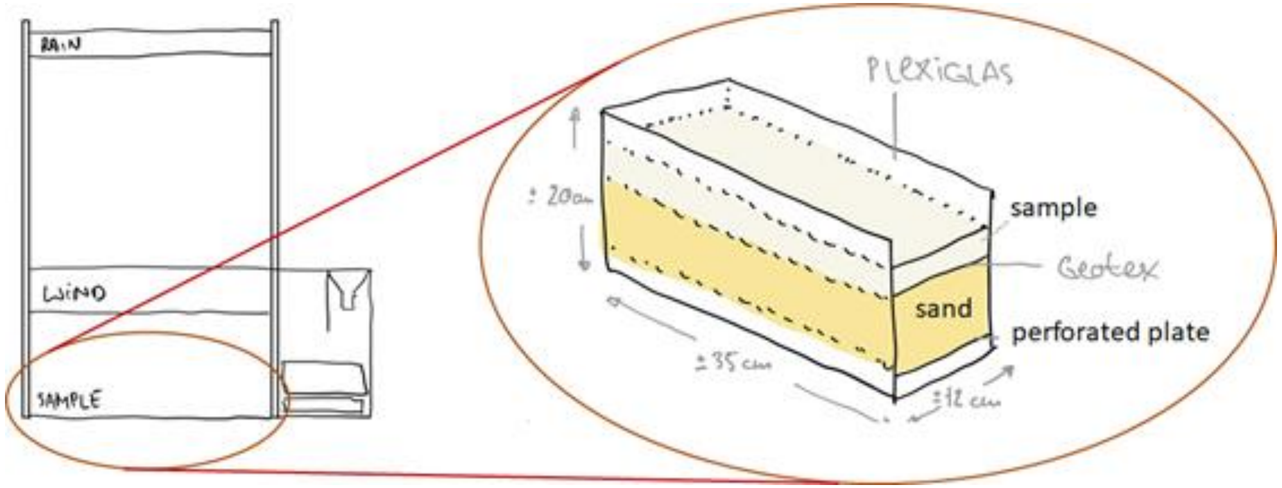
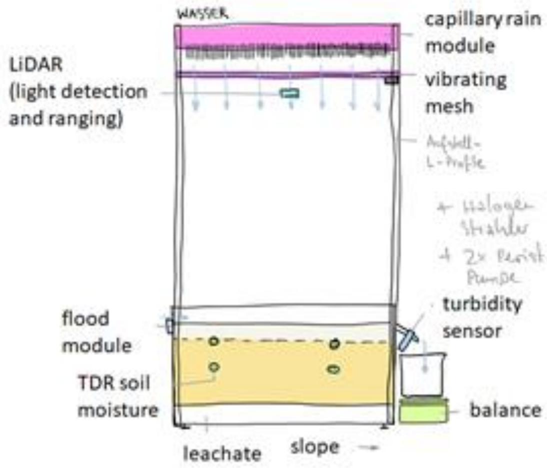
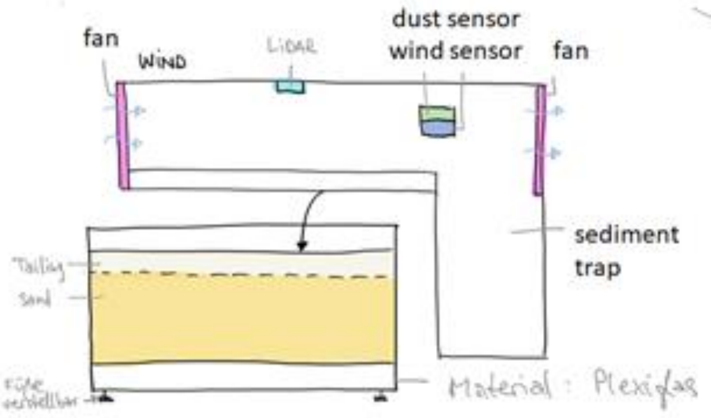
Erosion stability (no standard classification for mining residues)







Self designed setup for the determination of dustemission and water erosion

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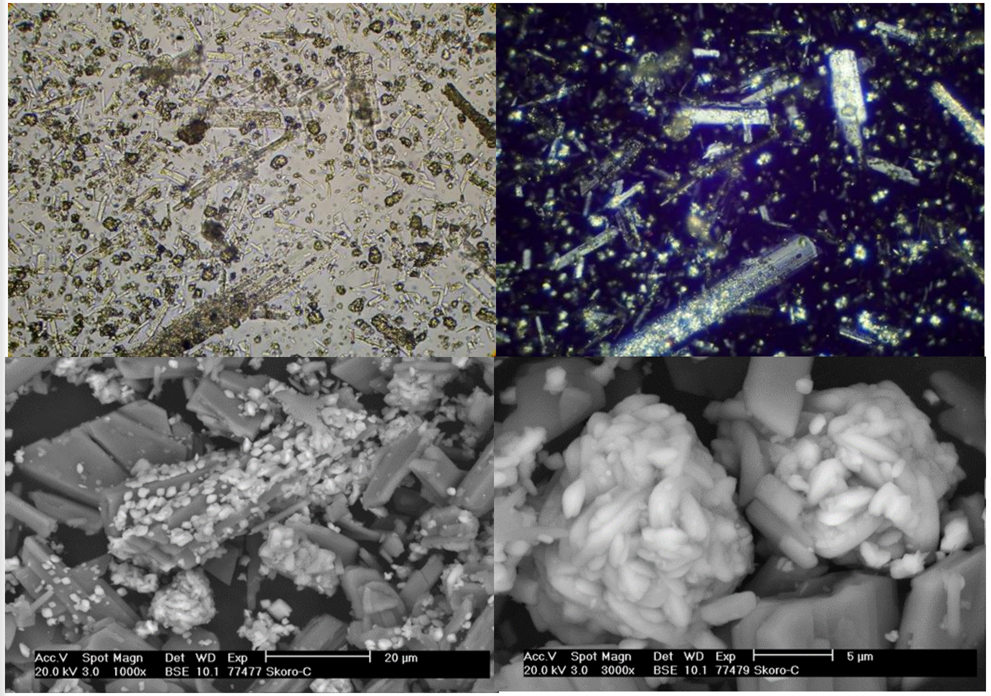
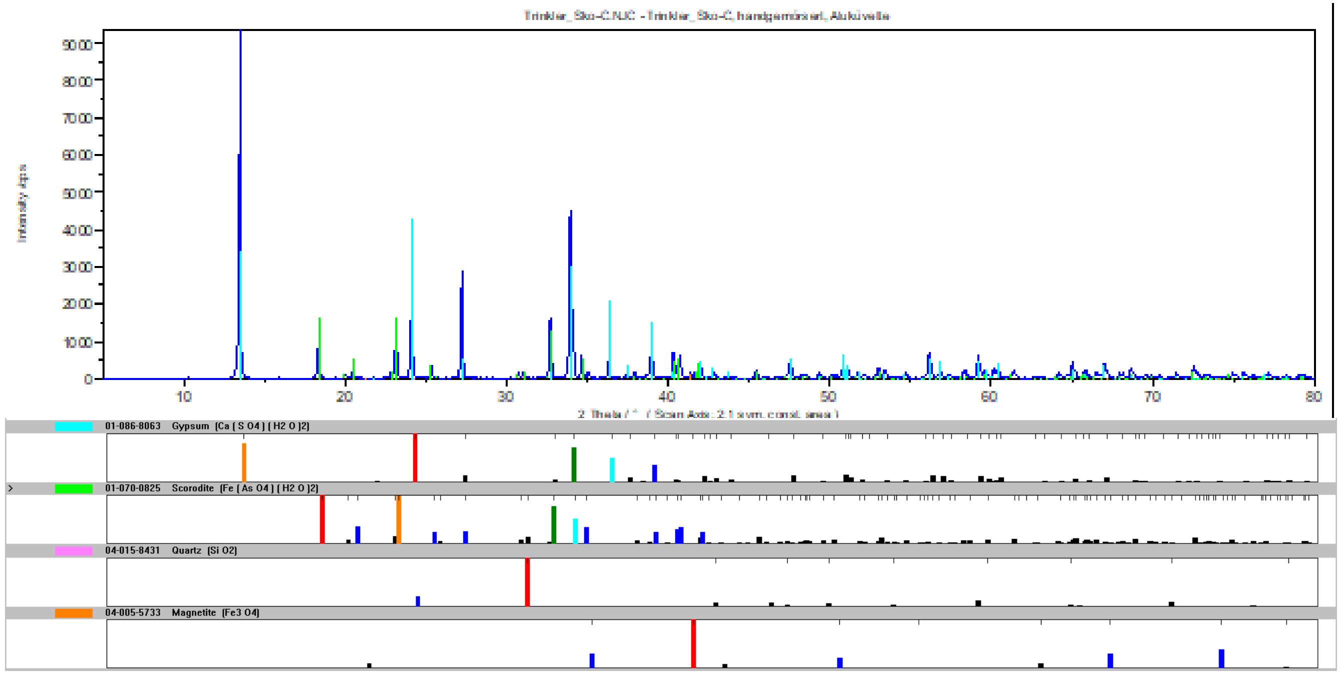
Residue stabilization – mineralogic characterization





- Scorordite ‚lumps‘ grow on gypsum crystals
- XRD pattern: 61 % w% gypsum, 39 % scrodite, traces of quartz and magnetite
- Due to high content of gypsum, lower solubility of As compared to pure Scorodite

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Mobilization - Conclusion

- Calama-Scorodite classifies by both arsenic leachate concentration and solid content as dangerous waste
- Leachate concentrations at constant pH of 4 exceed values required for surface mine waste storage
- Further tests(column leaching tests) will be performed for verification/ test of stabilization measures
- Erosion rate assessment is planned in a microerosion analyzer (design Prof. Jackisch, TU BAF, Flow and transport modelling in the geosphere)
- Wind erosion rates can be classified by allowed dust emission rates according to the german anti-pollution law
- Water erosion is most relevant with respect to runoff and leachate concentrations

Contact

Thanks for your attention!

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Metso:Outotec

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