Remediation Technologies and Water Treatment Operations

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Challenges and opportunities in the treatment and management of arsenic in the mining industry in Chile,
International seminar, Pontificia Universidad Catolica de Chile, 8 June, 2017

WISMUT project

- 1946 - 1990, SDAG WISMUT world's no. 4 uranium producer; major foreign uranium supplier to the Soviet Union (~ 216,000 tonnes of U from 20^{+} deposits)
- 1991, German government new company owner; remediation of one of the most extensive uranium-mining legacies in the world (largest European environmental remediation programme)

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- 7 production complexes, with more than 1,000 objects:
  - 5 underground mines (~ 80 million m^3 excavation volume)
  - 1 open pit (~ 84 million m^3)
  - 2 processing plants, 10 TMF (160^+ million m^3 tailings)
  - 60^+ waste rock piles (325 million m^3 WR)
  - 3,700 hectare operational areas with contaminated facilities

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Wismut remediation activities

- Safe closure of underground mines and controlled mine flooding
- In-situ stabilization or open Pit disposal of mine waste
- Tailings dewatering & stabilization
- Vegetated soil covers on tailings and waste rock
- Dismantling of surface structures, decontamination and site clean-up, disposal of contaminated material into containments
- Environmental monitoring & maintenance
- Water treatment and safe management of residues

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Wismut water treatment

- Mine flooding since 1991; water treatment since 1995 (until 2040)
- 4 WTP‘s for mine drainage, 2 WTP‘s for TMF seepage and pond water
- Prevailing water treatment technology: modified lime precipitation
- Upcoming technologies: ion exchange, GFH sorption, membrane filtration
- Discharge limits for U, As, ^{226}-Ra, heavy metals, Fe, Mn, SO_4, salt
- Treatment capacity of individual plants 100 - 700 m^3/h (max. 1,200 m^3/h)
- Total throughput ~ 20 million m^3/a
- Total residue volume ~ 25.000 m^3/a, treatment sludge stabilization after dewatering by cement addition (to increase physical and chemical stability)
- Residue deposition on company storage sites






Arsenic retention in lime precipitation plants

- 0.1 – 2 mg/l arsenic in mine and TMF seepage water
- Site specific regulatory limits10 – 100 µg/l

-airation (~ 5 m^3/m^3)
-limewater (~ 0.05..0.9 kg/m^3; stepwise, pH ~ 9-10)
-$KMnO_4$ (~ 1 g/m^3)
-$BaCl_2$ (~ 0.1 kg/m^3)
-$FeCl_3$ (~ 0.1 kg/m^3)
-flocculation aid
-HDS

- gas exchange, mixing
- oxidation of As, Fe, Mn
- precipitation of ironhydroxide sludge containing As, U, Ra, heavy metals

Ronneburg WTP, 850 m^3/h

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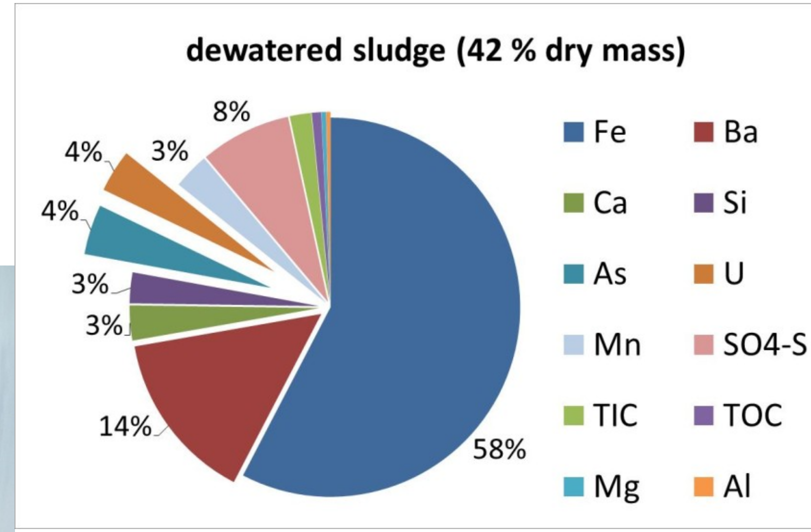
Arsenic retention in lime precipitation plants

Sludge separation and dewatering
- sedimentation tanks
- chamber filter presses, centrifuges)
  (30 – 50 wt% solid content)



Schlema WTP, 1,200 m³/h

Sludge stabilization (physical, chemical)
- cement / ash / CaO addition
 (~ 0,5 kg cement / kg sludge)
- crumbly substrates, monolithes

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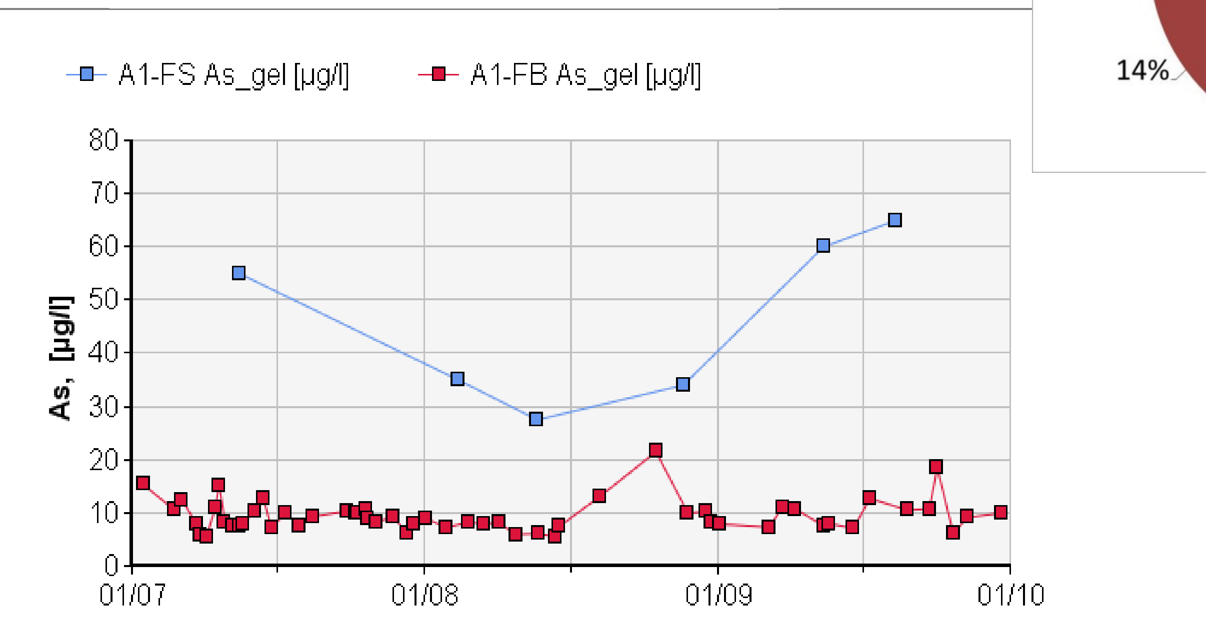
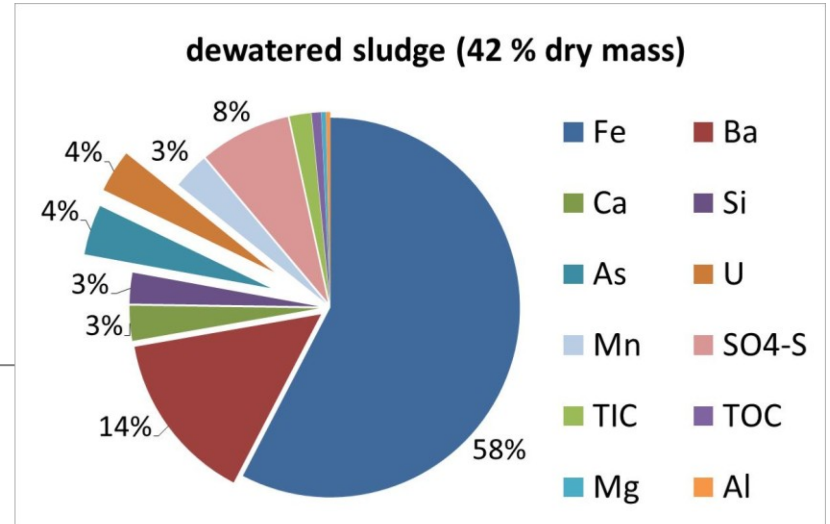
Arsenic retention in lime precipitation plants

1:10 leaching tests
blue: dewatered treatment sludge
red: stabilized treatment sludge





Schlema WTP, 1,200 m³/h

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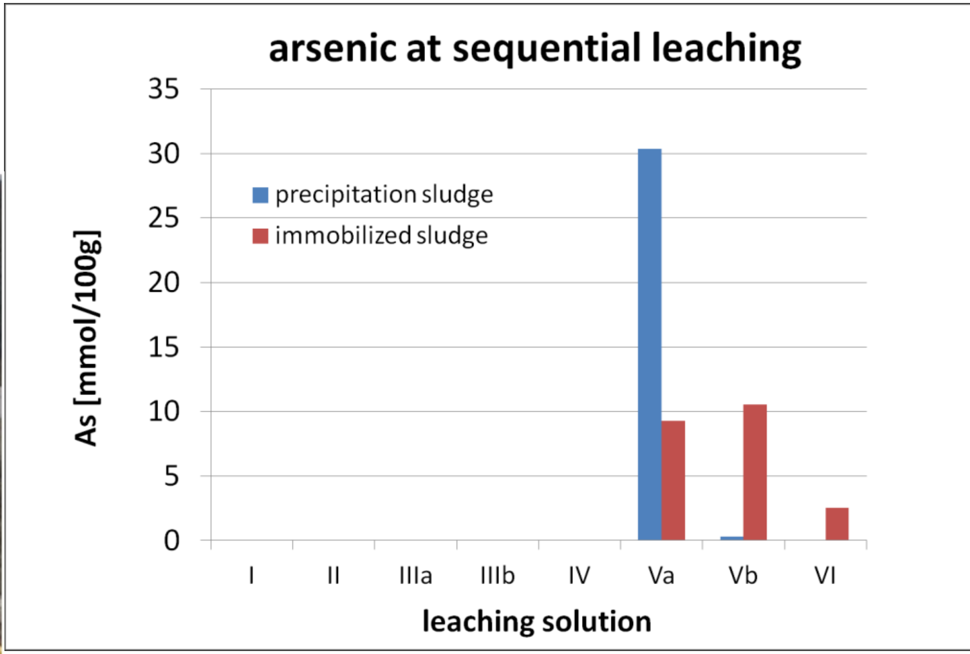
Arsenic retention in lime precipitation



leaching solution	binding form of leached contaminants
I	water soluble form
II	cation exchangeable form
IIIa	carbonates, specific bonds
IIIb	easily reducible minerals
IV	organic complexes
Va	poorly crystalline Fe-oxyhydroxides
V	crystalline Fe-oxides
VI	residual fraction (silicates, sulphides)

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Limitations in biochemically reduced mine water

Poehla mine water chemistry

SO_4 < 5 mg/L
U < 20 µg/L

pH = 7 – 7.5
E_H = 10 - 100 mV (CH_4, H_2)

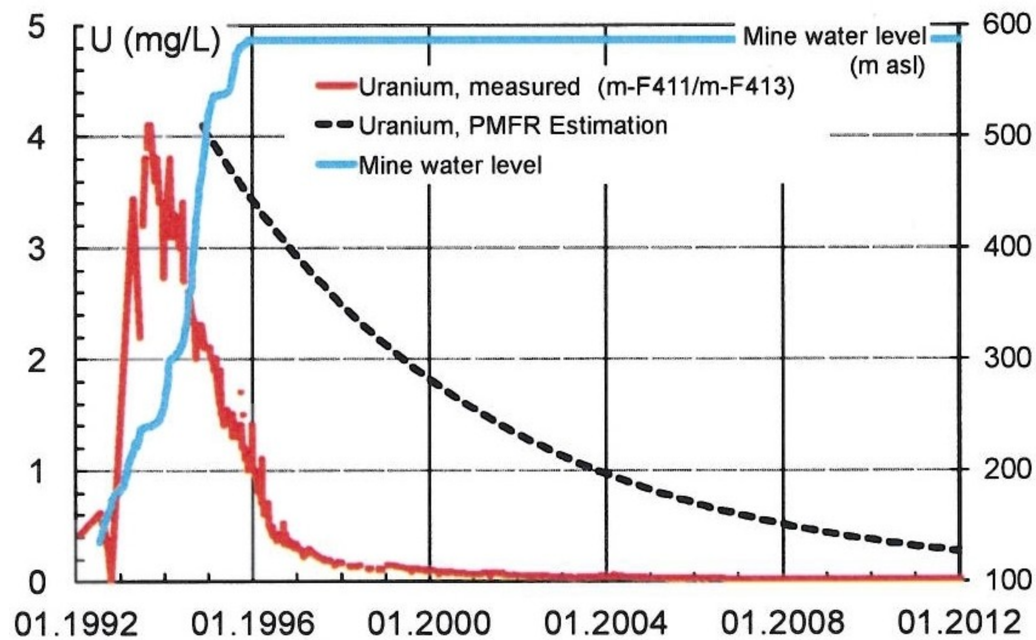
Fe = 5 mg/L (Ca, Mg, Na, HCO_3)
As = 2 mg/L

Pohla mine water microbiology

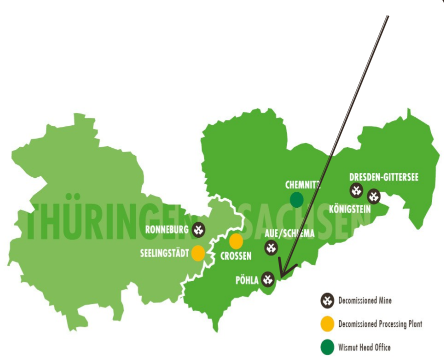
Sulfuricurvum spp., Sulfurovum spp., Syntrophus spp., Desulfurivibrio spp.

Candidatus Methanoperedes, Methanoregula, Methanobacterium

Patinella spp., Acremonium spp.



Uranium concentration in mine water Poehla (Paul et al., 2013)



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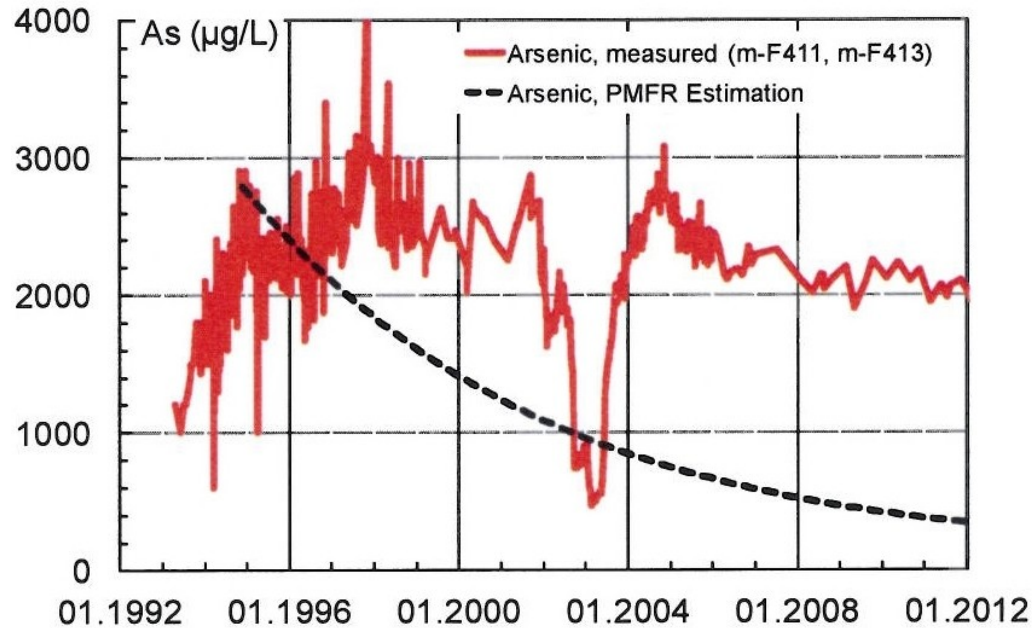

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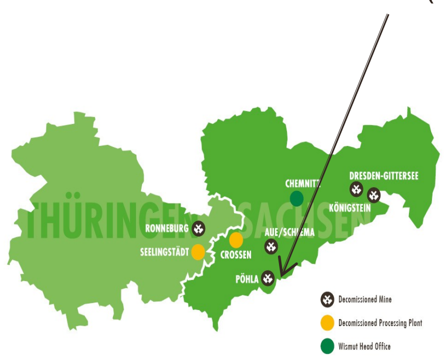

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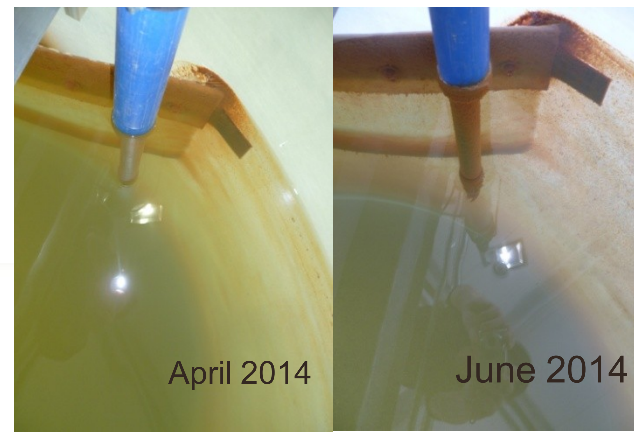
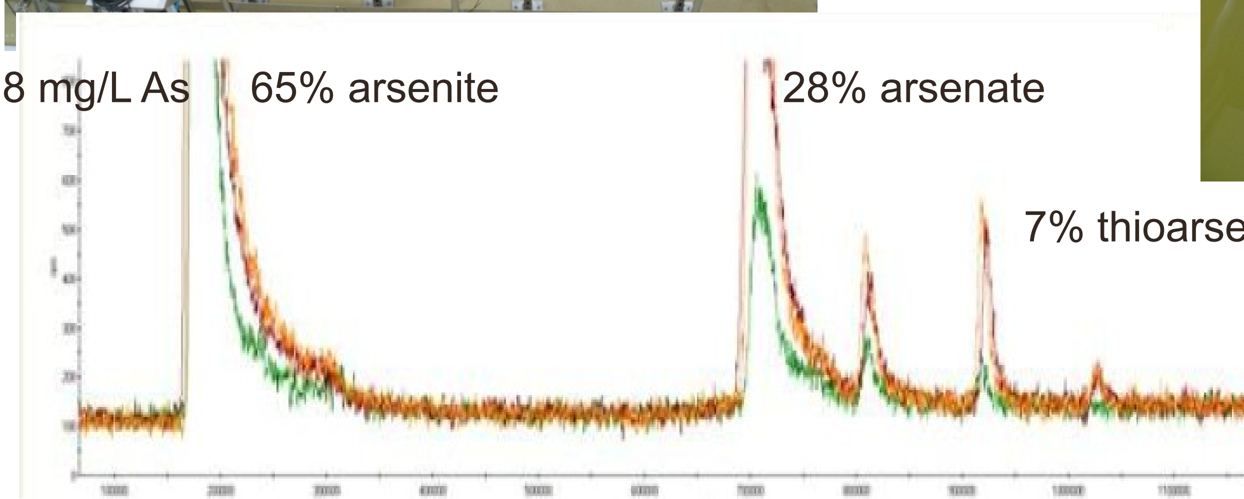
Limitations in biochemically reduced mine water

- reduction of ferric iron dosed as precipitation salt
- presence of reduced arsenic species
- hampered flocculation
- poor sludge quality
- insufficient arsenic fixation





HPLC-GC-MS-Analysis of dissolved arsenic in Poehla mine water (B. Planer-Friedrich, University Bayreuth)

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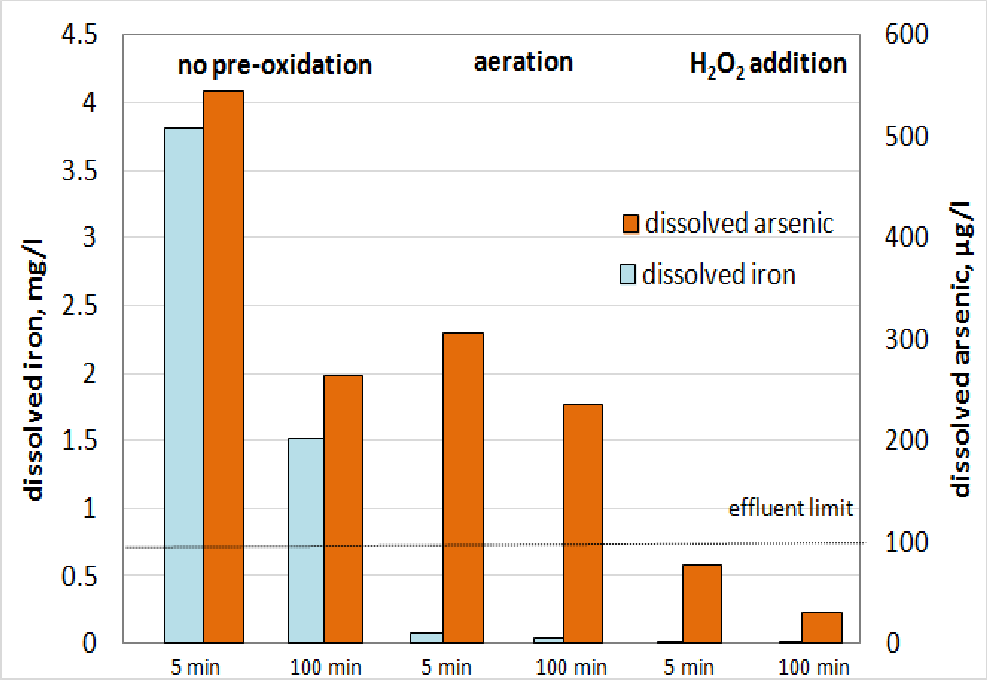
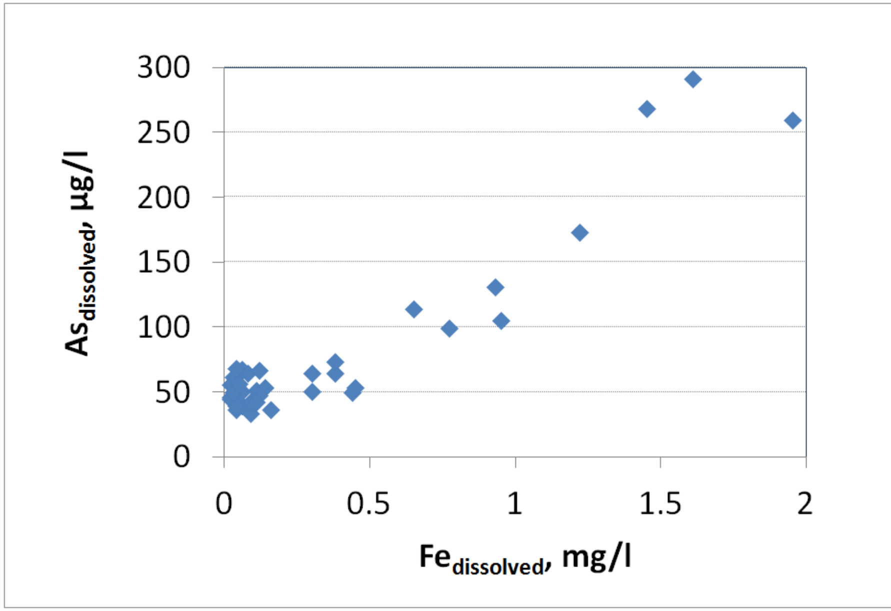
Limitations in biochemically reduced mine water

Lab tests improvement iron flocculation



Field results



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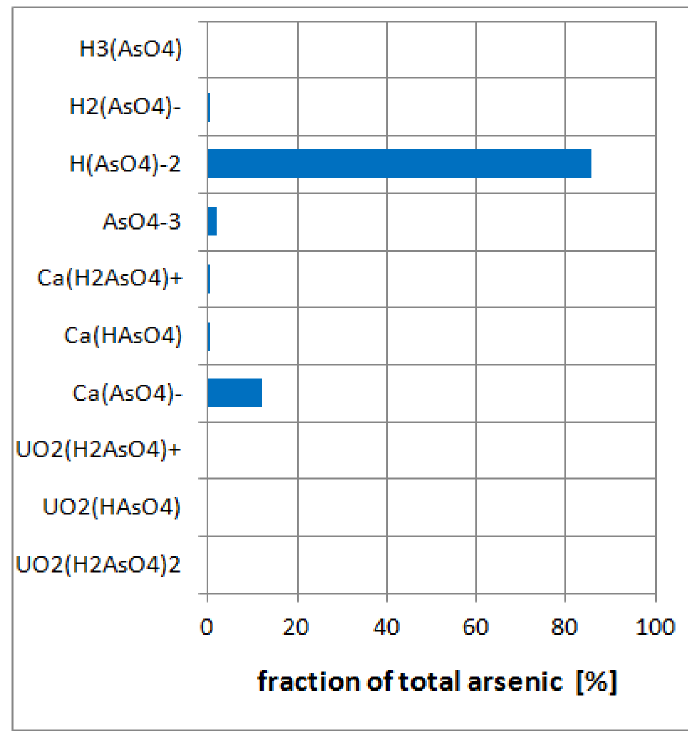
Arsenic retention by granular ferric hydroxide

mg/l	pH	U	As	Na	HCO_3	CO_3	Cl	SO_4
10/2014	9.1	4.7	0.5	1,360	1,350	161	419	1,750
03/2015	9.2	7.0	0.6	1,790	1,260	232	509	2,250



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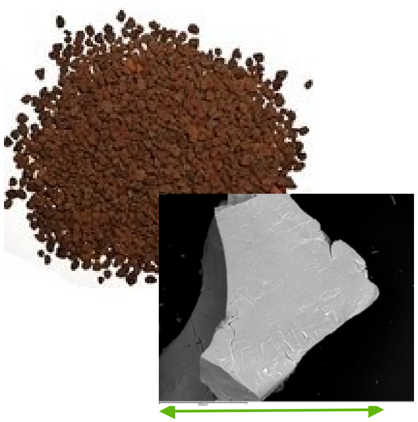
Arsenic retention by granular ferric hydroxide

Fixed bed adsorption of arsenic to GFH:

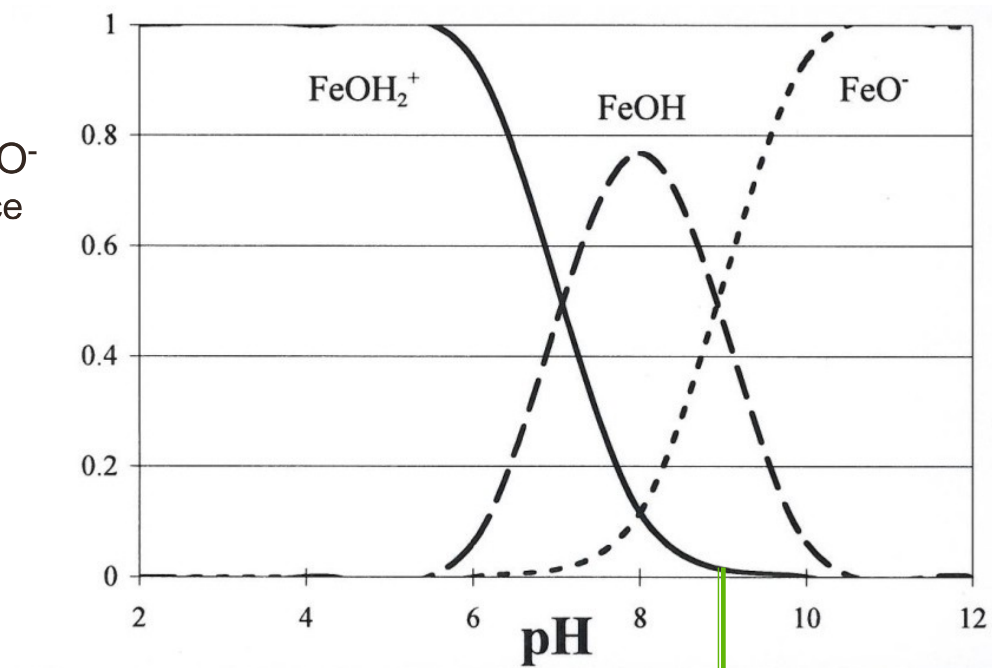
- ferrihydrite adsorption (iron-coprecipitation) BDAT for heavy metal removal from MIW
- GFH adsorption BAT for As removal in drinking water treatment
- waste water application studies for PO_4



0.5 mm

$FeOH^{2+}$, FeOH, FeO^-
(pH depending surface charge, pzc ~ 7-8)

Intraparticle surface diffusion
(sorption kinetics)



$H(AsO_4)^{2-}$
$Ca(AsO_4)^-$
pH ~ 9

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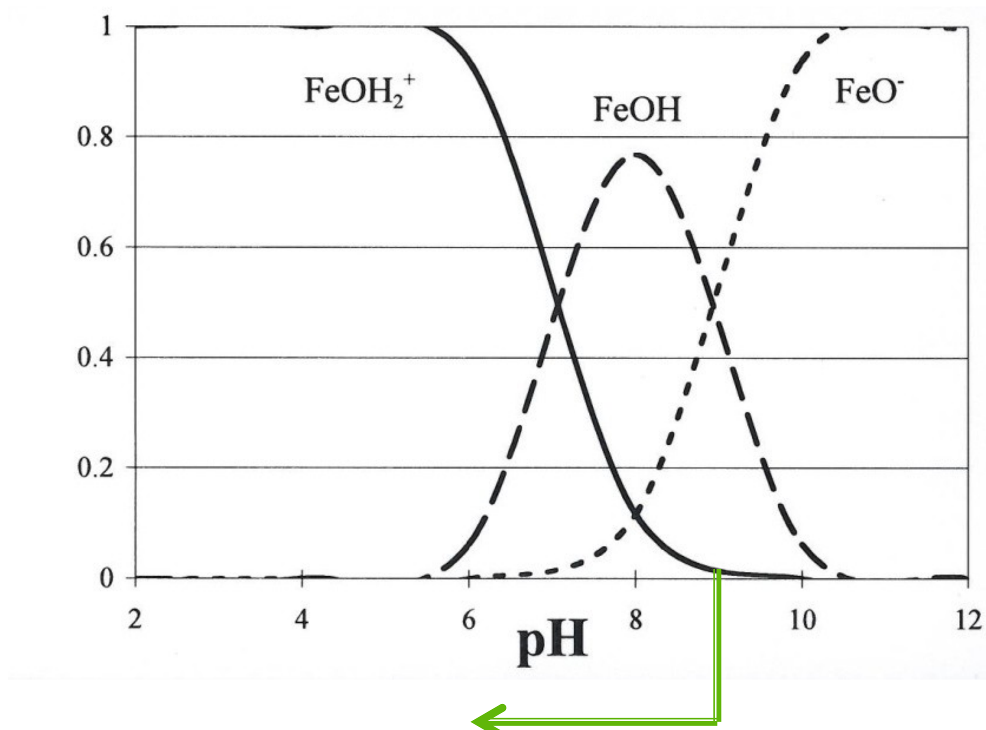
bed volume 5 ml, GEH,
velocity 10 BV/h, t_r 6 min



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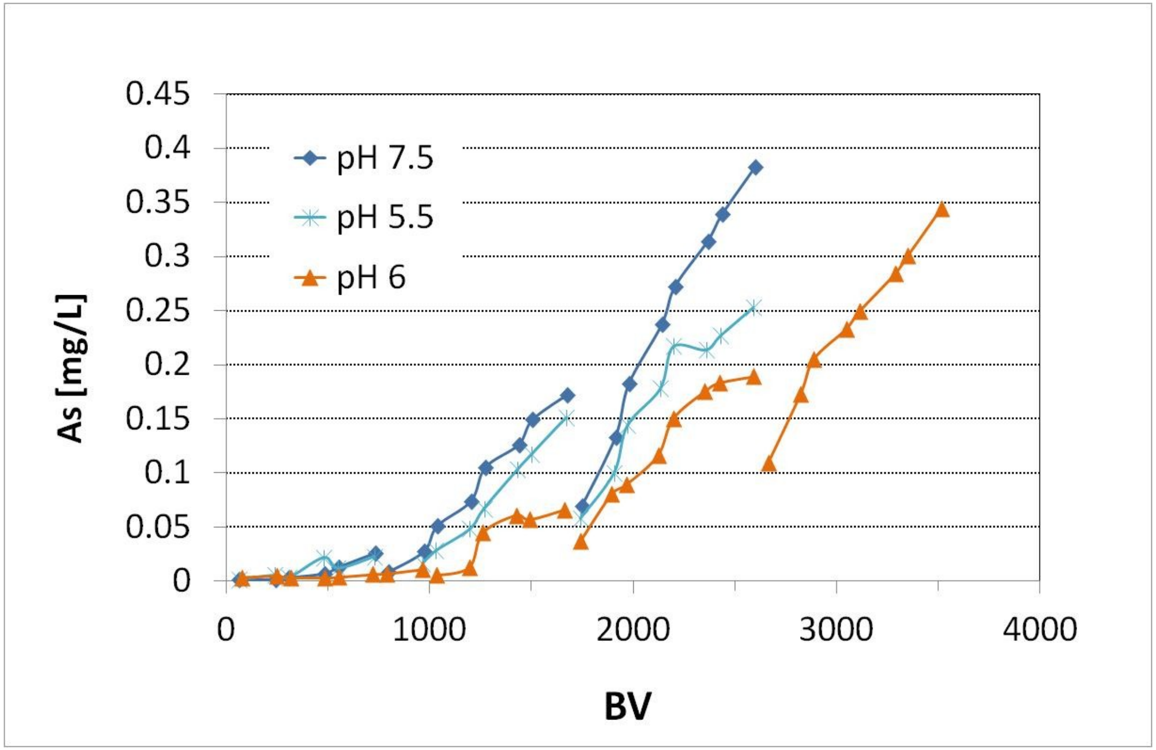
bed volume 5 ml, GEH (akaganeite, pzc 7.5-8.2), velocity 10 BV/h, t_r 6 min



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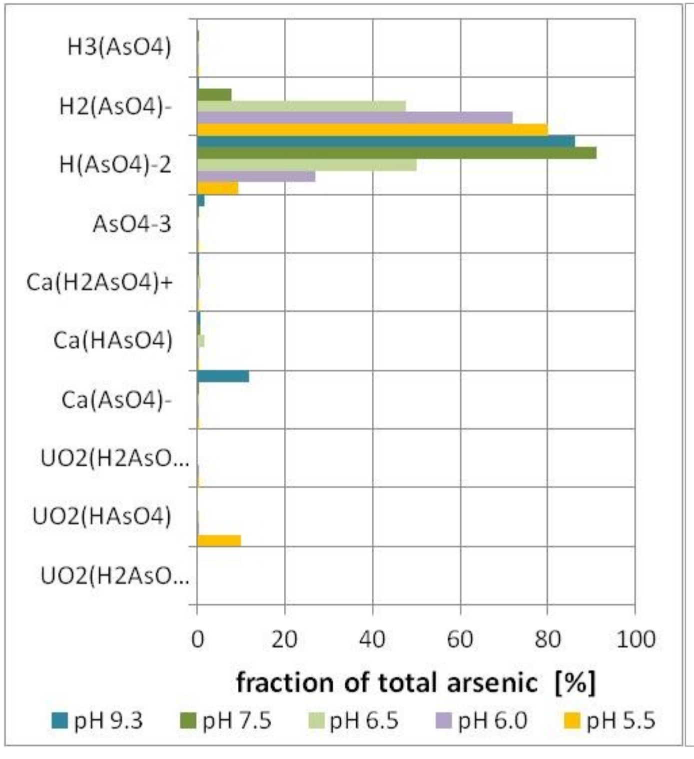

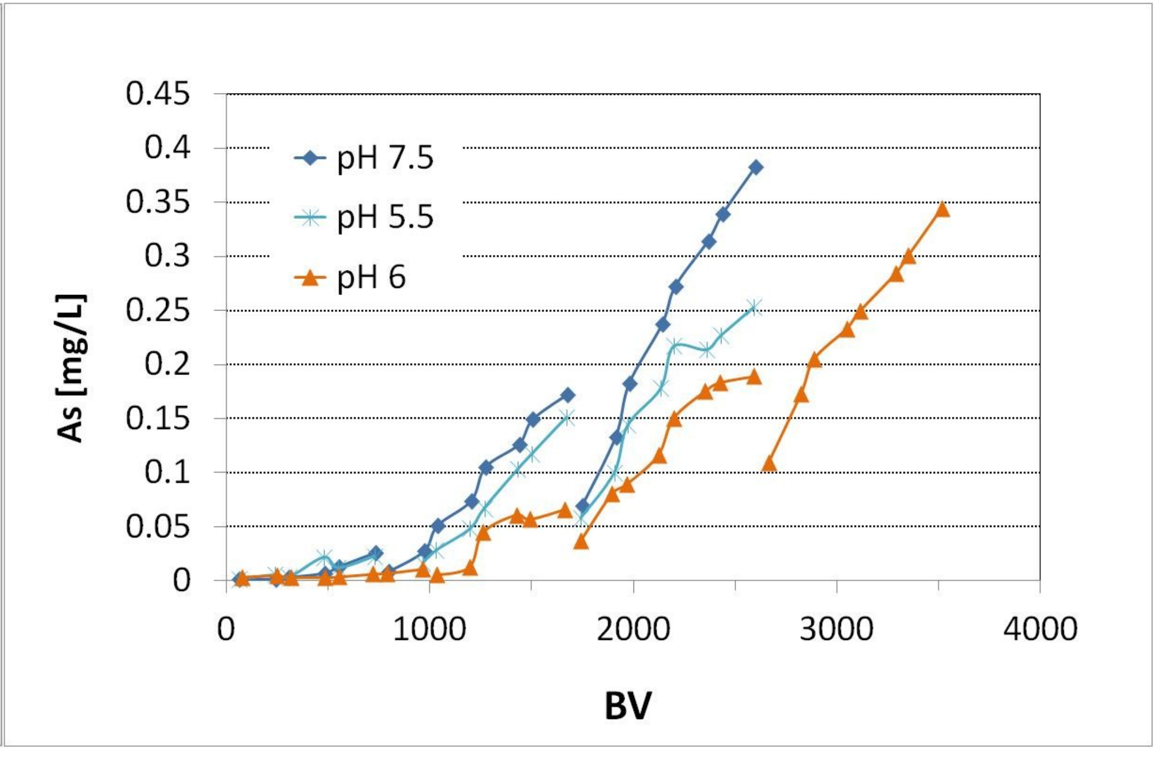

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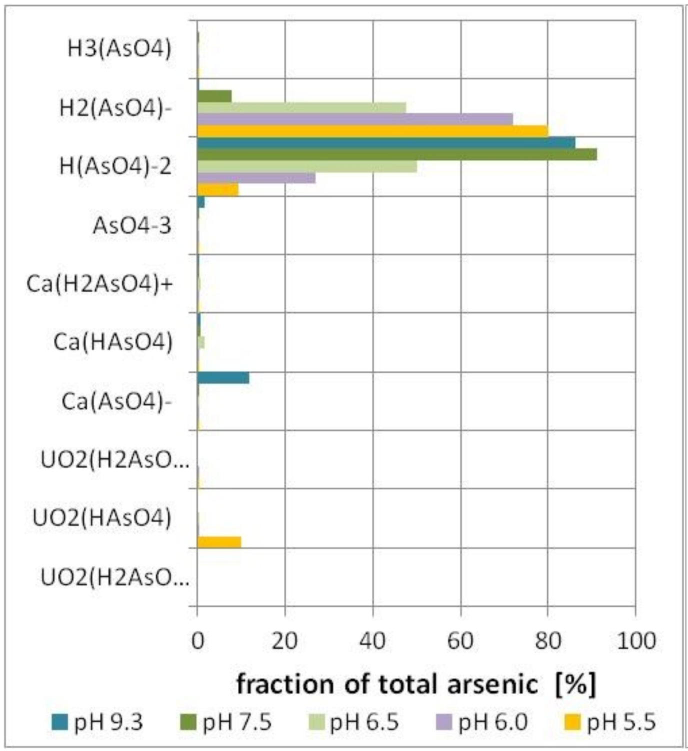

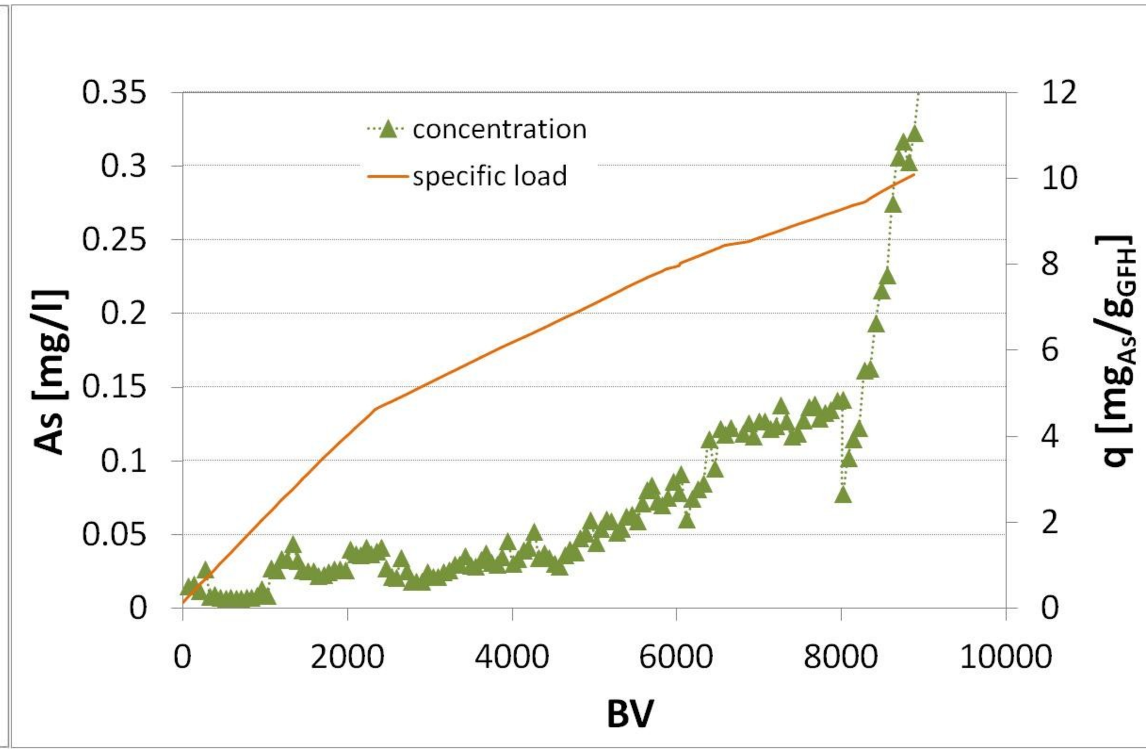

bed volume 5 ml, FerroSorp (ferrihydrite/calcite, pzc ~ 8), velocity 2.5 BV/h, t_r 24 min, pH 6

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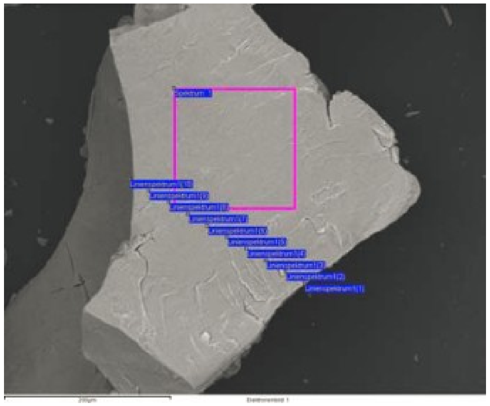
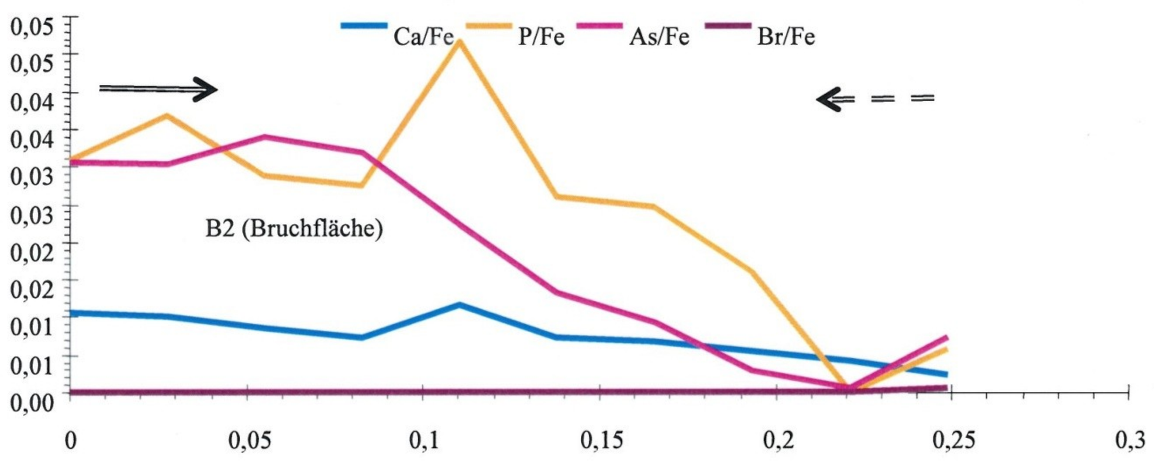
Results from Lab tests for TMF seepage water treatment:

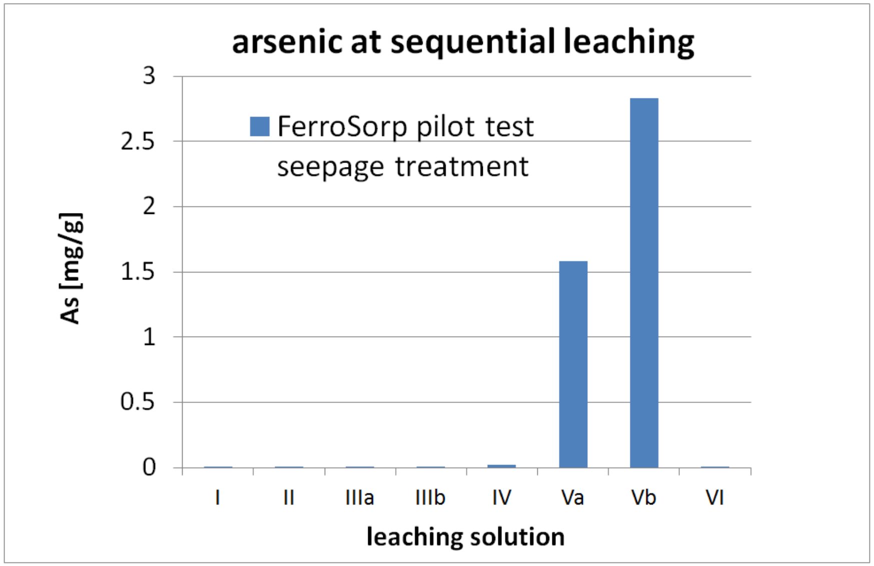
- pH = 6..6.5 to maximize negative charge of arsenic species and positive charge of HFO surface
- v = 2.5 BV / h to allow for intraparticle diffusion
- Specific load: 5 – 10 mg As / g GFH





R. Schöpke, Brandenburg University of Technology, Cottbus

As - binding stability at GFH



leaching solution	binding form of leached contaminants
I	water soluble form
II	cation exchangeable form
IIIa	carbonates, specific bonds
IIIb	easily reducible minerals
IV	organic complexes
Va	poorly crystalline Fe-oxyhydroxides
V	crystalline Fe-oxides
VI	residual fraction (silicates, sulphides)

1:10 leaching tests (pH-stat: 24 h, pH 4 and 11)

pH		4.0	11.0
EC	mS/cm	2.5	5.17
U	mg/l	0.0191	8.57
As	**mg/l**	**0.009**	**17.2**
K	mg/l	10.6	<25
Na	mg/l	174	1380
Mo	mg/l	<0.02	107
Mg	mg/l	48.5	4.1
Ca	mg/l	174	7.1
Fe	mg/l	<0.02	0.524
SO_4	mg/l	23	356
CO_3	mg/l	<5	864
HCO_3	mg/l	<5	981
TOC	mg/l	0.63	791

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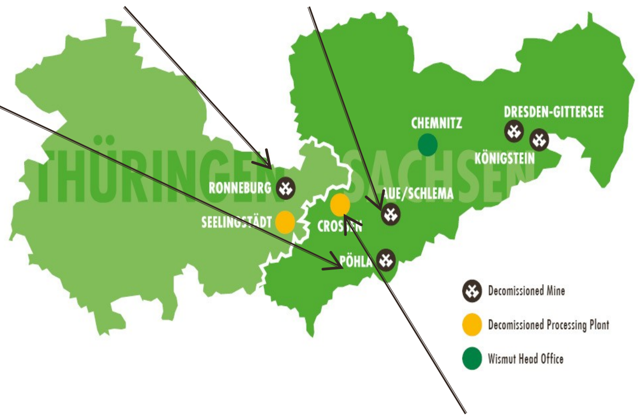
Summary WISMUT Arsenic Water Treatment

Lime precipitation plants

- BAT for arsenic removal from MIW
- Sorption and coprecipitation at ferric hydroxides
- Limitations in biochemically reduced mine water – pre-oxidation step required
- Stable As binding in precipitaiton sludge



GFH sorption filter plants

- BAT for arsenic removal from drinking water
- Sorption depends on pH and filter velocity – pH and velocity adjustment required
- Stable As binding at slightly acidic to slightly alkaline pH
- As mobilization at alkaline pH

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Thank you for attention!