Application of ferrates for removal of arsenic from groundwater A quarter-operating practical test

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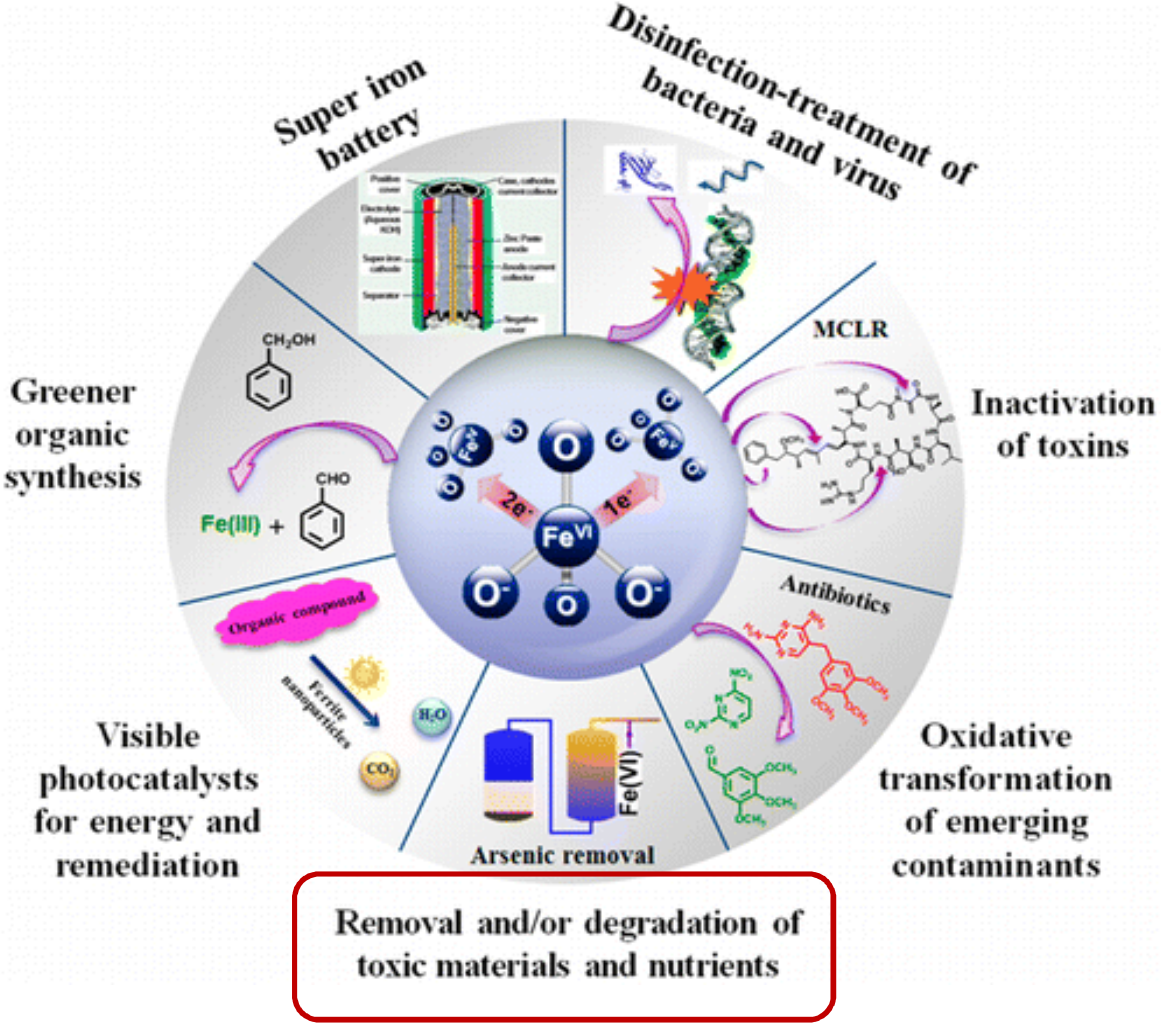
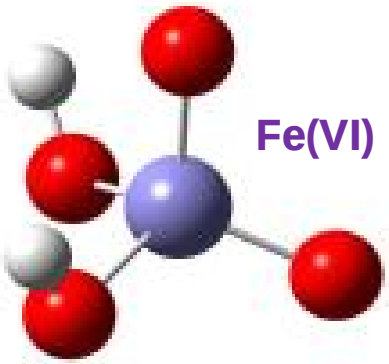
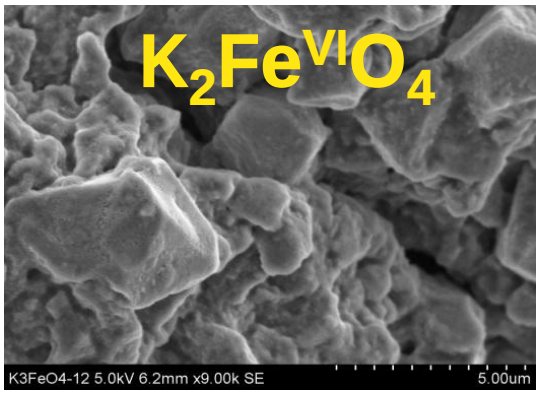
FERRATES –

What are they and what are they good for ?







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FERRATES –
What are they and what are they good for ?

- a general name for compounds of iron in high oxidation state - Fe(IV), Fe(V) and Fe(VI),
- highly oxidizing behavior, measured redox Eh + 850 mV
- reaction end products form non-toxic ferrous oxides and oxyhydroxides that can act as coagulants
- disinfection effect
- laboratory tests have confirmed an interesting application potential in the area of water treatment technologies
- In 2014 an affordable technology for production of ferrates for industrial application was successfully developed and implemented

FERRATES –
application for removal of arsenic from groundwater

- **Ferrate decomposition in water yields nanoparticles (as solid precipitates formed by nearly-amorphous g-Fe_2O_3 and g-FeOOH). Arsenic is adsorbed onto and partially incorporated into the structure of these nanoparticles within three to five minutes.**
- **Subsequently it is necessary to finely separate the resulting iron micro-flakes containing As.**

Czech legislation limits for drinking water (in Vyhl.252/2004 Sb.):

As	**Max. admissible concentration**	**10 µg / l**
Fe	**Limit value**	**200 µg / l**

Two different potential sources of drinking water with naturally elevated As content were investigated (site „MEZ“, site „KLU“). The distance between the sites is12 km.

1. site "MEZ": As 70 - 90 µg / l

2. site "KLU": As 90 - 100 µg / l

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Site MEZ

Site KLU

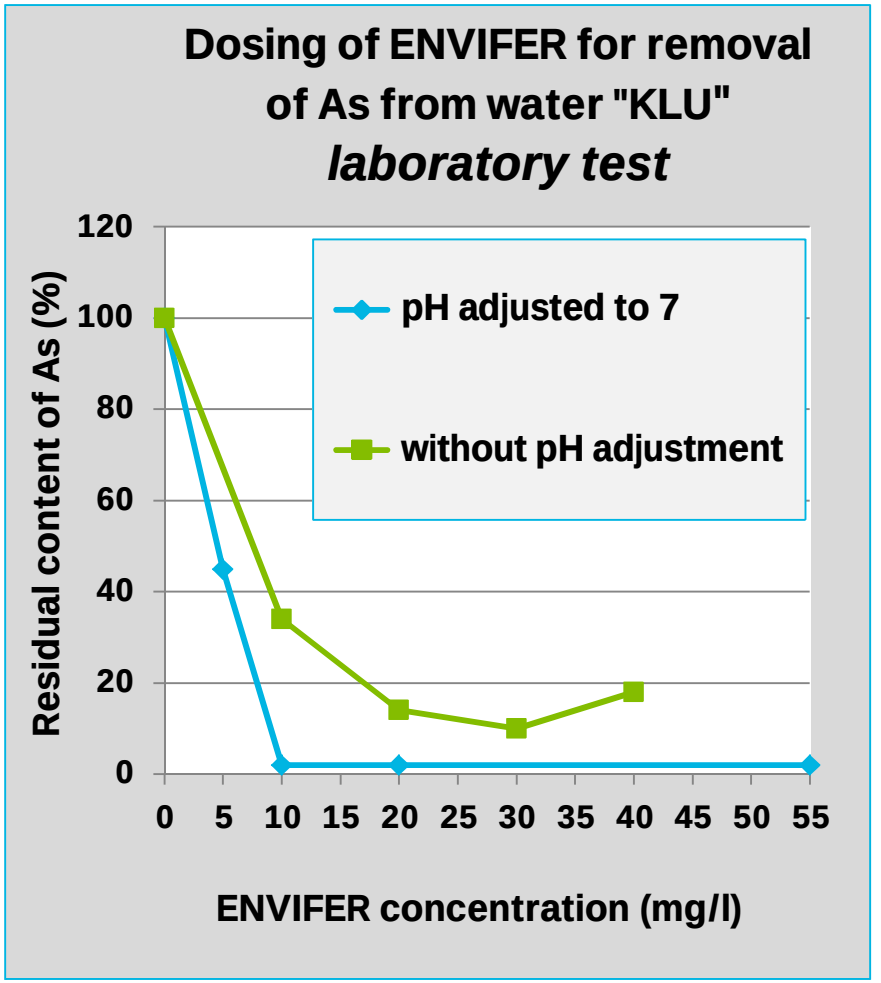
FERRATES – characterization of material used = ENVIFER, Batch LAC 019

ENVIFER Batch LAC 019 dry product by Mössbauer spectroskopy & AAS	
$KFe(III)O_2$	29 ± 3 %
$K_3Fe(V)O_4$	50 ± 5 %
$K_2Fe(VI)O_4$	6 ± 2 %
K_2O	< 3 %

The difference of upto 100 % is due to the content of oxidic impurities (approx. 5-10%), the accumulation of measurement errors and the content of unidentified components with different stoichiometry

ENVIFER Batch LAC 019 water solution 0.5 g/L by UV-VIS spectrometry, 510 nm		
Time	Absorbance at 510 nm	$K_2Fe(VI)O_4$
1 min	0,98	33,35%
24 hrs	0,1	3,40%

FERRATES – an optimal dosing for investigated groundwater



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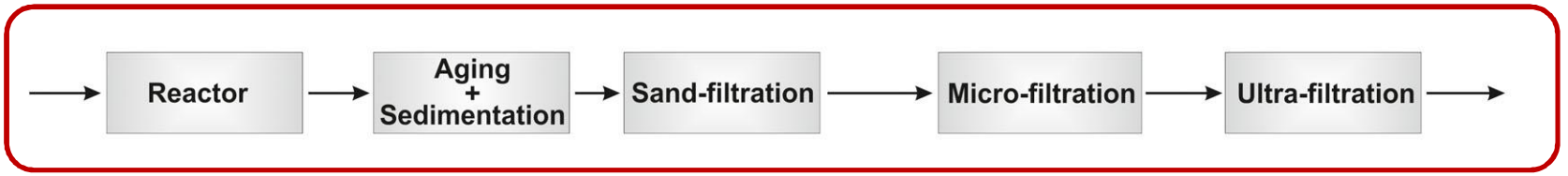
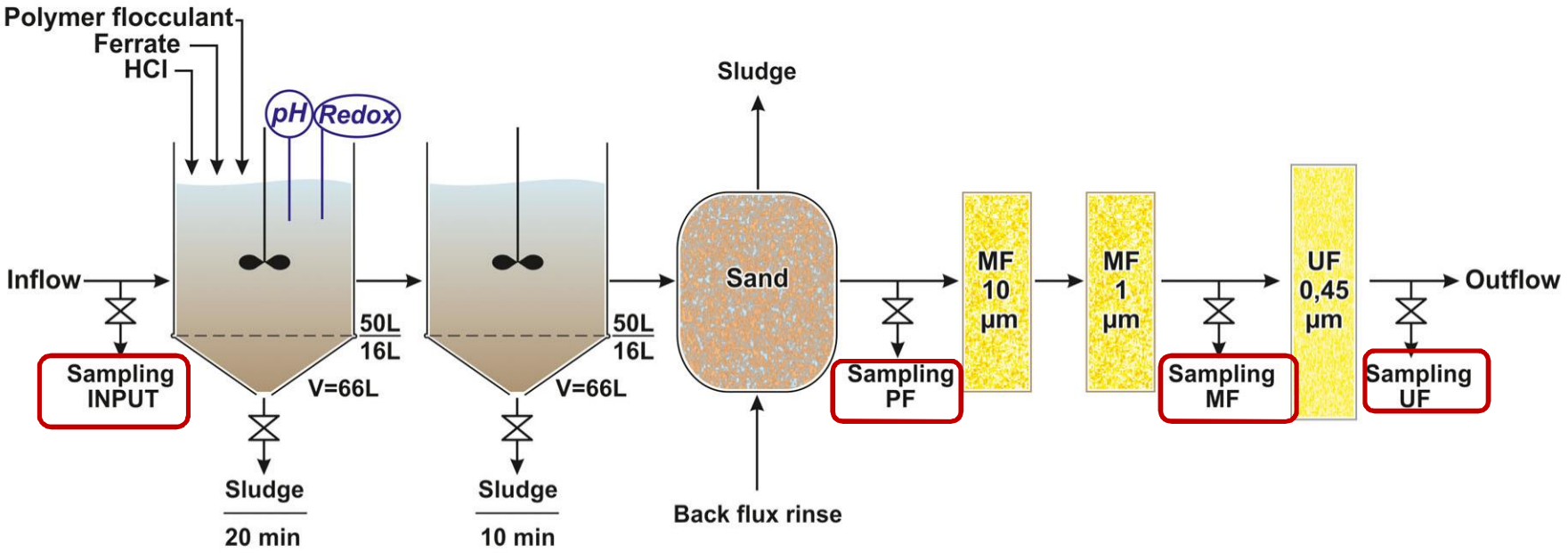
TECHNOLOGICAL LINE FOR ARSENIC REMOVAL FROM GROUNDWATER BY FERRATES

Approx. 100 L/hr





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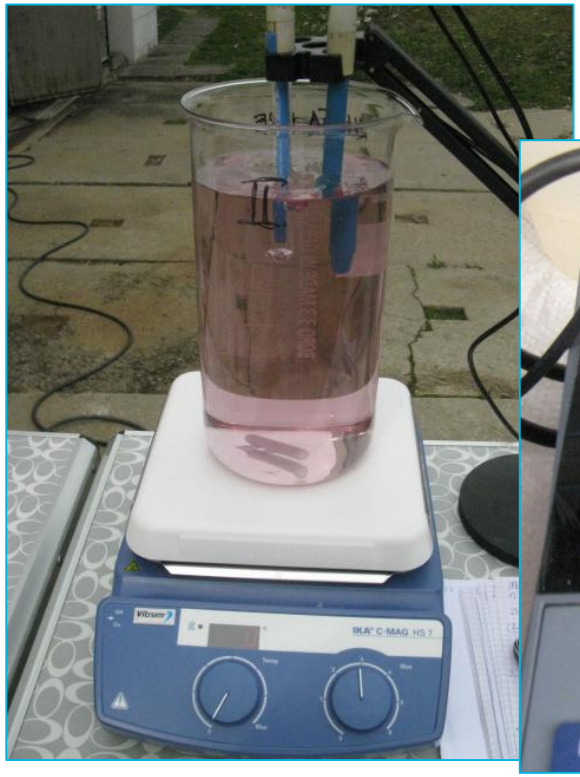
Pilot technology field testing - As removal from GW by ferrates, 100 L/h (2 volumes per hour)

1. **Reactor**
2. **Sedimentation**
3. **Sand filtration**
4. **Microfiltration 10 µm**
5. **Microfiltration 1 µm**
6. **Ultrafiltration 0,45 µm**

- **50 L water**
- **Ferrate (ENVIFER) dosing:**
  5-10-15-20 mg/L
  (***250-500-750-1000 mg/50L***)
- **Polymer flocculant**
- **HCl**

Laboratory tests *on-site*: final verification of ferrates dosing with fresh groundwater



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Technology test *on site*: measurement and sampling

Pilot trial

Pilot technology field testing 100L/hr

1. on site laboratory verification for reagents dosing: ferrate, HCl, flocculant
2. duplicate testing on the technology unit for each ENVIFER (ferrate product) concentration (5; 10; 15; 20 mg /L). Sampling points: input + water after sand filtration (PF), microfiltration – (MF), & ultrafiltration (UF)
3. Independent laboratory analysis of final results for As, Fe, pH, microbiology by an accredited laboratory

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Results of duplicated field testing

	As INFLOW (µg/L)	As OUTFLOW after ultrafiltration (µg/L)							
		Ferrate ENVIFER batch 019 5 mg/L		Ferrate ENVIFER batch 019 10 mg/L		Ferrate ENVIFER batch 019 15 mg/L		Ferrate ENVIFER batch 019 20 mg/L	
		A	B	A	B	A	B	A	B
Site MEZ	89	11	17	<5	<5	<5	<5	<5	<5
Site KLU	102	NA	NA	13	17	12	<5	<5	5

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Arsenic removal by specific filtration phases

	Site MEZ, ENVIFER 10 mg/L		Site KLU, ENVIFER 15 mg/L	
	As - residual content	As removal by specific filtration phase	As - residual content	As removal by specific filtration phase
	%	%	%	%
INPUT	100	0	100	0
after PF	49,5	50,5	61,3	38,7
after MF	11,9	37,6	42,4	18,9
after UF	0	11,9	0	42,4

- Chemical composition of water influences :
  - relative degree of As removal by specific filtration phase, so there are differences between sources (spiked pure water data unreliable)
  - size of separated microflakes
- Aging of water also influences results

KLU site with 15 mg/L ENVIFER: analytical data

Sample	As	Fe	K	pH
	µg/L	mg/L	mg/L	-
Detection limit	*0,0050*	*0,0020*	*0,0150*	*1*
A – INPUT	102	0,0035	2,5	7,44
A – after PF	69	1,26	9,03	6,59
A – after MF	24,9	0,252	8,73	7,35
A – after UF	12,5	0,0814	8,75	7,22
B - INPUT	102	0,0035	2,5	7,44
B – after PF	62,5	1,3	9,26	7,39
B – after MF	43,2	0,784	9,37	7,37
B – after UF	<0,005	0,0746	9,85	7,25
50 L water KLU + 750 mg ferrate + flocculant + HCl				

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Microbiological data before and after ENVIFER dosing (10-15-20 mg/L)

Microorganisms	Sample	INPUT	UF_ No floculant 10 mg/L	UF_B 10 mg/L	UF_B 15 mg/L	UF_B 20 mg/L
Clostridium perfringens	CFU/ 100 mL	0	0	0	0	0
Coliform Bacteria	CFU/ 100 mL	100	0	0	0	0
Enterococci	CFU/ 100 mL	57	0	0	0	0
Escherichia coli	CFU/ 100 mL	0	0	0	0	0
Microorganisms cultivated at 22°C	CFU/mL	3300	18	0	3	0
Microorganisms cultivated at 36°C	CFU/mL	2900	10	0	0	0

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Waste products following processing of 516 L of groundwater with 0,1 mg/L As

1. Sand filtration

1a) wash water

Standard washing procedure was used – 5x sand filler volume
(e.g. 35 L of sand ~175 L of water)
Sampling: SUM – the entire volume of wash water sampled

1b) sludge

No measurable amount of sludge was captured from wash water

Microfiltration and ultrafiltration

No measurable decrease of pressure was detected before MF and UF

Wash water from sand filter – chemical analysis		
ALS Laboratory	Unit	SUM
COD-Mn	mg/L	1,11
Suspended solids (105°C)	mg/L	10,2
As total	mg/L	0,119
Fe total	mg/L	2,74
As dissolved	mg/L	0,0105
Fe dissolved	mg/L	0,0125

- Arsenic still firmly bound to Fe-microflakes
- Wash water is not a hazardous waste following microflake removal

Ferrate costs – current

- 1 kg of ENVIFER: 80 EUR
- ENVIFER dosing : 10-15 g/m^3 of treated groundwater
- ENVIFER price: 1,0-1,1 EUR/m^3 of treated groundwater

Method limitation

- A higher phosphorus concentration decreases Arsenic removal

Conclusions

- **The efficiency of the proposed technology was confirmed on two different groundwater sources with a naturally increased arsenic content of 10 × the drinking water limit. In both cases, the arsenic output concentration complied with the drinking water limit (<10 μg / L). The optimal dose of ferrate (= ENVIFER LAC 019) for the first water was 10 mg/L (10 g/m3), for the second 15 mg /L (15g/m3)**
- **The mobile unit with a capacity of 100 L / hr is suitable for simulating full-scale application. It provides investors with sufficient confidence for the construction of a functional full-service facility**
- **The volume of waste sludge with arsenic is very small compared to a traditional flocculation method**
- **Wash water, after removing the flakes, is not a hazardous waste. Arsenic is still firmly bound to Fe-microflakes in sludge**
- **The outgoing water from the test unit is microbiologically compatible with drinking water requirements**

Thank you for your kind atention