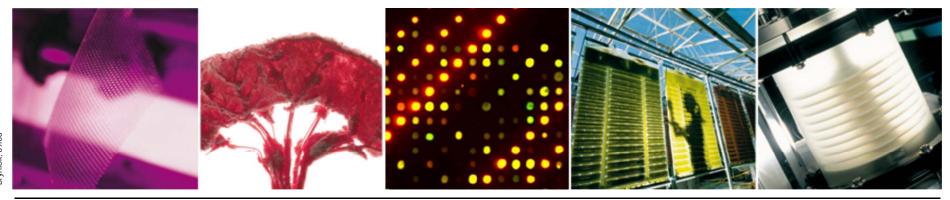
### Contaminated Sediments – an Ecological Bomb

# Removal and Reuse of Metal Sulfides from Water Using a Fixedbed Anaerobic Loop Bioreactor

Dr. Werner Sternad and Dr. Dieter Bryniok

Water Workshop WATER QUALITY - Novi Sad, 3rd September 2008





#### **Sediment Treatment**

- dredging
- separation
  - gravel
  - sand
  - silt
  - clay
- de-watering
- storage
- further treatment
- utilization
- final disposal



### Heavy Metals in Veliki Backi Canal Sediments at Vrbas



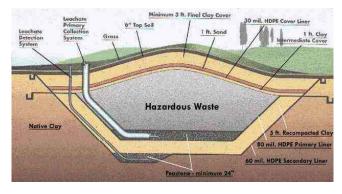
Most important contaminants: heavy metals, dissolved in water as metal ions and/or precipitated in the sediment as metal sulfides and other hardly soluble salts



metal	average concentration (mg/kg)	maximum concentration (mg/kg)
Zn	1700	8500
Cu	280	620
Ni	74	170
Cr	200	1200

analyzed by University of Novi Sad, Faculty of Sciences, Department of Chemistry

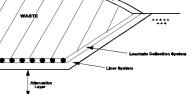
## Storage and Final Disposal of Sediments



oxidation of metal sulfides and mobilization of metals

- leachates formed by
  - humidity of the sediment
  - rainfalls
- abiotic oxidation (e. g. by O<sub>2</sub> or NO<sub>3</sub>-), favored by
  - low pH value
  - aeration and dissolved oxygen
  - carbonic acid
  - organic matter
  - light

$$2 \text{ FeS}_2 + 7.5 \text{ O}_2 + 3 \text{ H}_2\text{O} -> \text{Fe}^{3+} + 4 \text{ SO}_4^{2-} + 2 \text{ H}_3\text{O}^+$$
  
 $\text{FeS}_2 + 14 \text{ Fe}^{3+} + 24 \text{ H}_2\text{O} -> 15 \text{ Fe}^{2+} + 2 \text{ SO}_4^{2-} + 16 \text{ H}_3\text{O}^+$ 



- bacterial oxidation (e.g. Bdjejui jocbdjmvt! gfsppyjebot)
- formation of sulfate favors additional abiotic oxidation

### Avoiding the Release of Heavy Metals to the Environment

#### Sludge dredging and treatment:

- avoid oxygen transfer
- treatment of water before release back to the canal

#### Storage of the sediments:

- disposal site with liner system and leachate collection and treatment
- prevent oxidation and leaching
  - covering the disposal site
- alternatively: treatment by bio-leaching of metals an treatment of the leachate
  - rinse the disposal site
  - aeration and pH adjustment
  - supply with organic substrates and HCO<sub>3</sub>-
- utilization of the sediment after treatment e. g. as building material

#### Final disposal at a safe landfill for hazardous wastes:

disposal site with water-tight cover, liner system, leachate collection and treatment

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### Precipitation of Metals in a Fixed-bed Loop Bioreactor





Project at the Fraunhofer IGB

Treatment of wastewater from the automotive industry containing cooling lubricants and heavy metals in high concentrations

The concentration of the dissolved metals in the water phase had to be reduced below the legal limits

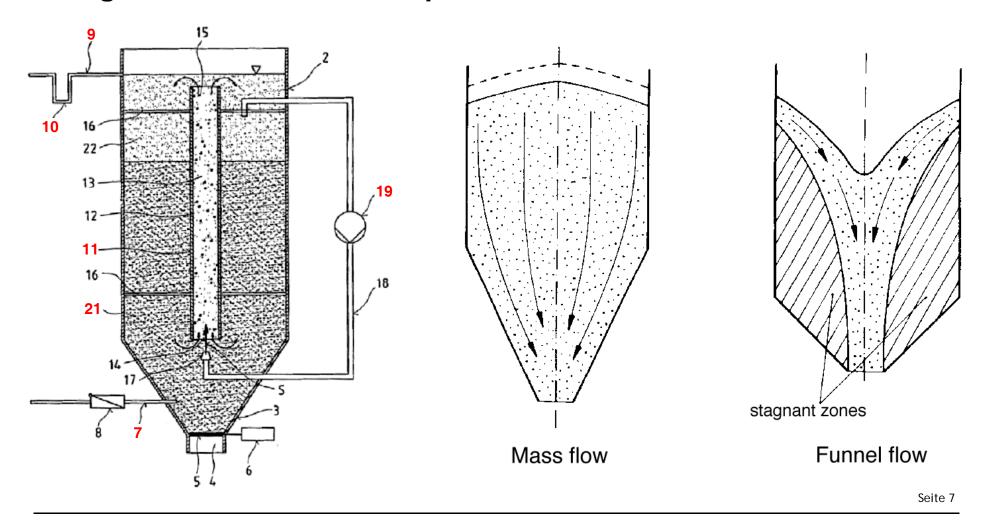
#### Solution:

Bio-precipitation of metal sulfides with sulfate-reducing microorganisms in a fixed-bed loop reactor

Removal of precipitated metal sulfides from carrier particles



## Design of a Fixed-bed Loop Reactor (FBLR)





# **Fixed-bed Loop Reactors**







30 Liters

100 Liters

3500 Liters

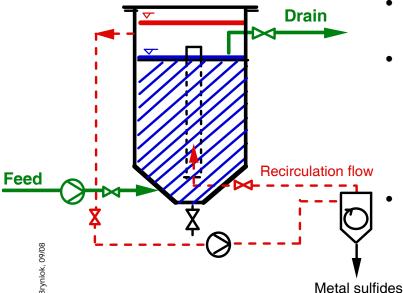
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#### Principle of the Fixed-bed Loop Reactor (FBLR) Process

- Wastewater is fed into the bottom of the reactor and passes through the fixed bed.
- Sulfate-reducing microorganisms sulfate to sulfide and dissolved metals to insoluble metal sulfides.
- The fixed bed is loaded with the crystallized metal sulfides.
- Conventional fixed-bed reactors would block in course of time.
- A pump periodically drives water from the top of the FBLR into the inner conveying pipe. The particles of the fixed bed are trasnsported to the top of the reactor. The resulting turbulence in the conveying pipe cleans the particles.
  - Metal sulfides are separated in the hydro-cyclone.



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## Scanning electron micrograph of an overgrown carrier





3000 fold 4000 fold

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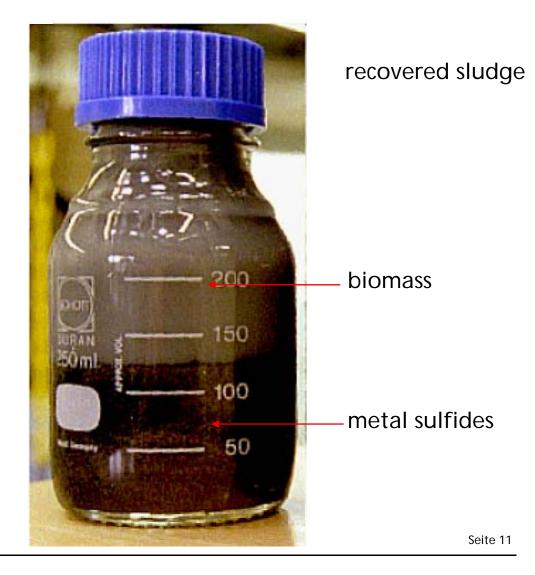


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# **Recovery of Metal Sulfides**

hydro-cyclone

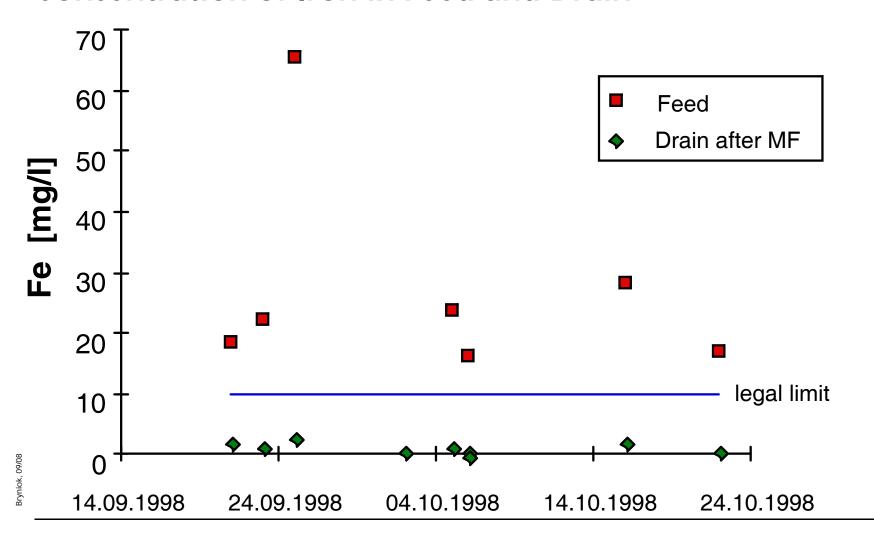




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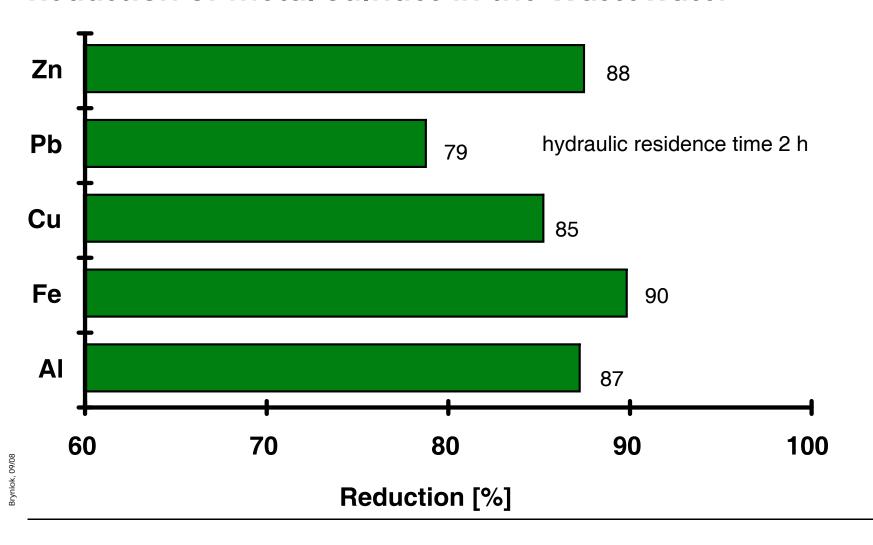


#### Concentration of Iron in Feed and Drain



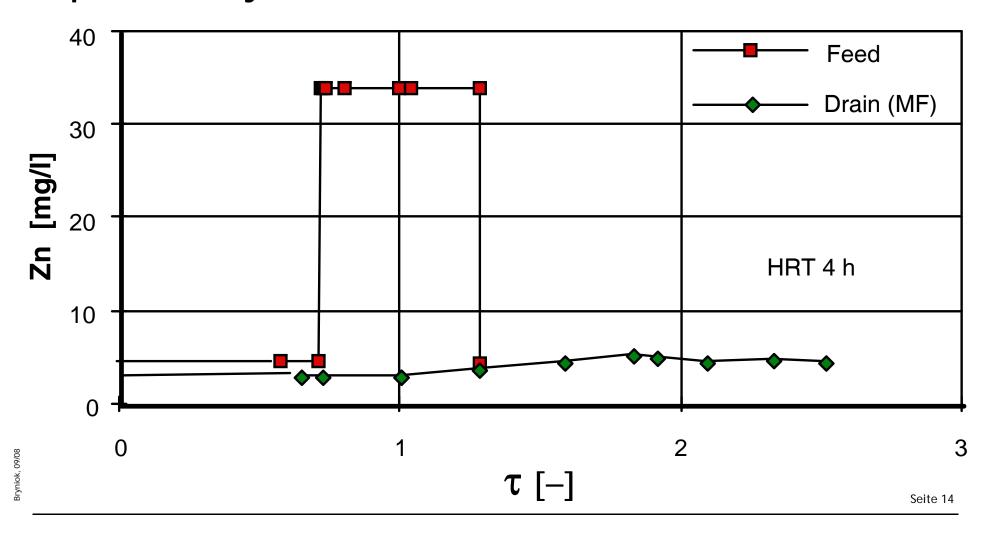


#### Reduction of Metal Sulfides in the Wastewater



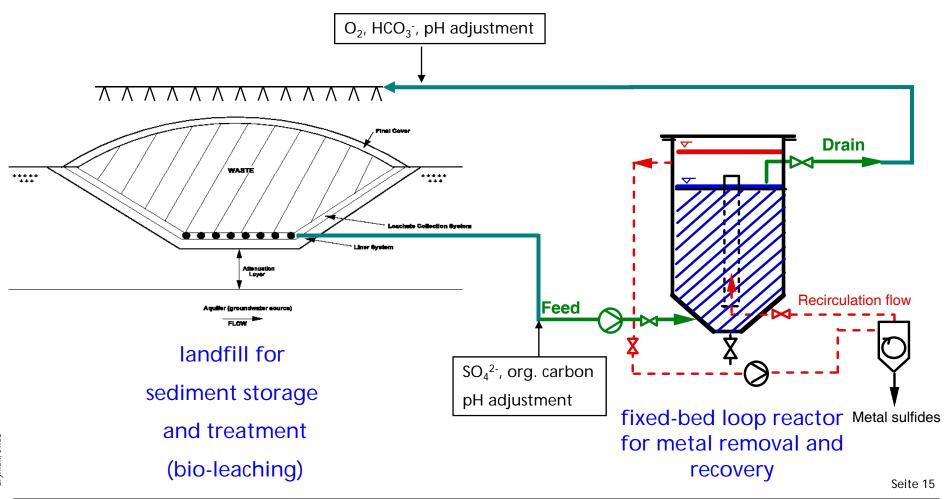


# **Impact Load by Zinc**





## Perspective: Bio-leaching and Recovery of Heavy Metals





## Thank you very much for your attention!



rvniok, 09/08