Application of whey to prevent re-oxidation of secondary iron sulfides in a passive anoxic in-lake reactor – success and failure

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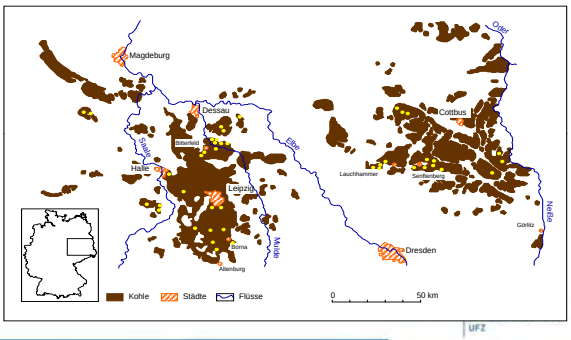
Outline

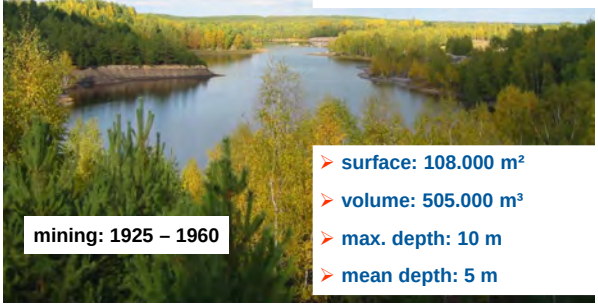
- Brief Introduction
  - Experimental approach for remediation/neutralization
  - Passive anoxic in-lake reactor (enclosure)
- Aim and Scope of Investigations
  - How to prevent re-oxidation ?
- Results
  - Water chemistry
  - Sediment geochemistry
- Summary and general conclusions

Lignite mining districts of East Germany



Lignite Mine Pit Lake PL-111

- pH: 2.6
- EC: 2500 µS/cm
- SO_4: 1300 mg/L
- Fe: 150 mg/L



mining: 1925 – 1960

- surface: 108.000 m²
- volume: 505.000 m³
- max. depth: 10 m
- mean depth: 5 m

Biological alkalinisation

Sulfate reduction

Iron reduction

Precipitation of iron-sulfide

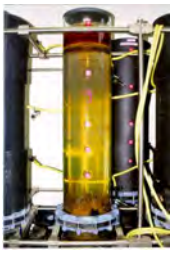
$9\ CH_2O + 4\ FeOOH + 4\ SO_4^{2-} + 8\ H^+ \rightarrow 4\ FeS + 9\ CO_2 + 15\ H_2O$

$15\ CH_2O + 4\ FeOOH + 8\ SO_4^{2-} + 16\ H+ \rightarrow 4\ FeS_2 + 15\ CO_2 + 25\ H_2O$

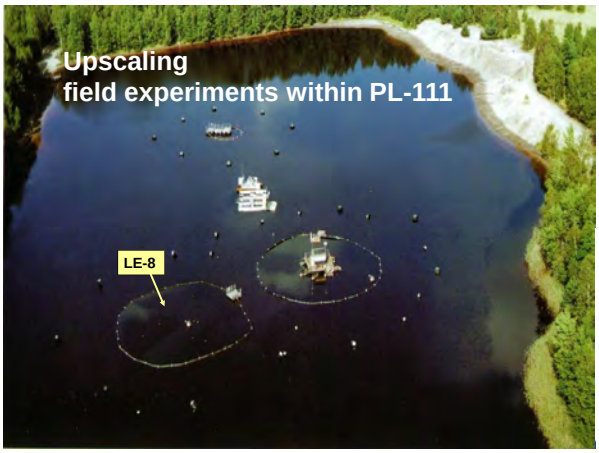
Anderson and Schiff, Can.J.Fish.Aqu.Sci. 1987

Experimental approach – upscaling

Looking for an appropriate and cheap organic substrate



Frömmichen et al. ES&T 2003, 2004



Application of substrate June 2001

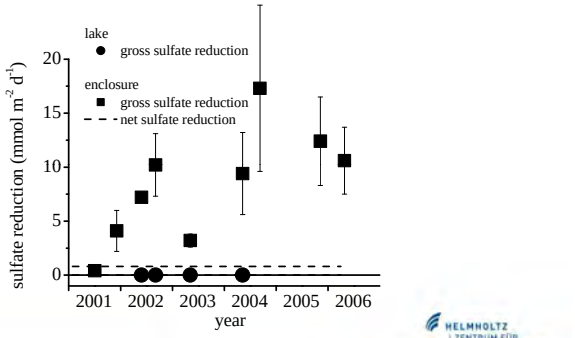
Enclosure LE-8: 6 m depth, 30 m ø = 4500 m³

4.2 t Carbokalk (10.7 mol TOC m^{-2})

6 t Straw = 400 straw bales (8.5 kg m^{-2} = 436 mol TOC m^{-2})

Bozau et al. JGE 2007; Geller et al. JGE 2009

sulfate reduction netto << brutto

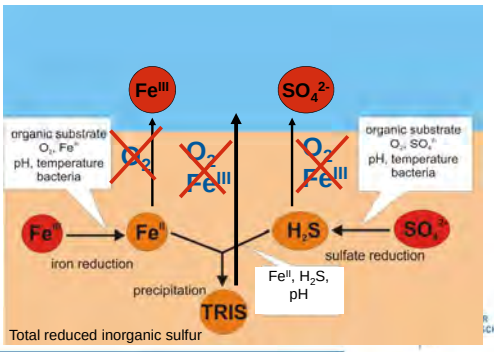


Neutralisation rates

	volume (m³)	neutralisation rate (eq m^{-2} a^{-1})
Laboratory column	0.088	15
Small enclosure	26	10
Big enclosure	**4500**	**1.7**

Scale effect ?

No sustainable precipitation of FeS/FeS_2 ➔ Re-Oxidation



Application of whey

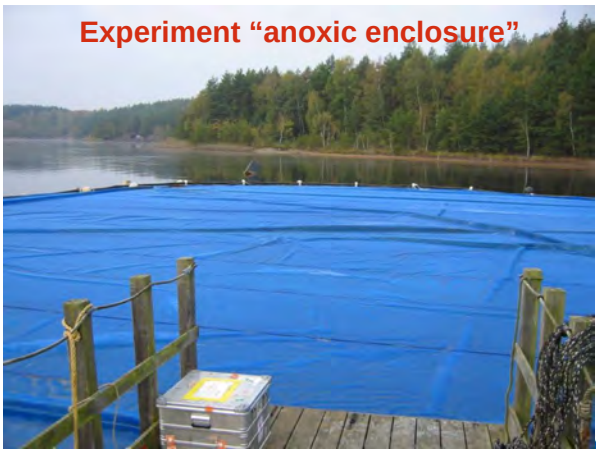
Date	kg
9.10.2007	50
6.11.2007	50
23.4.2008	50
6.8.2008	50
22.10.2008	50

C-concentration of whey = 380 g Kg^{-1}

50 kg whey = 2,3 mol m^{-2} = 0,34 mmol C L^{-1}

for elimination of O_2	41,6	kg
for elimination of iron	88,6	kg
in total	130,3	kg

Experiment “anoxic enclosure”



Aims of experiment

- Is it possible to generate an anoxic water column within an enclosure and to maintain the anoxic conditions ?
- Is it possible to reduce all ferric iron within the water in this way ?
- Will the rate of neutralisation and the stability of the secondary sulfides be increased under the anoxic water conditions ?

Material and Methods

bi-weekly monitoring of physicochemial parameters (T, pH, Eh, O_2, EC) and selected chemical data (Fe-II, Fe-III, SO_4)

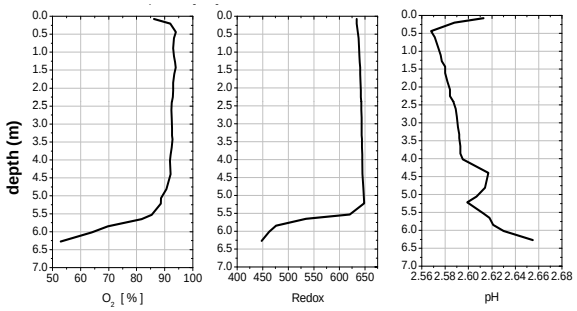
status of sediment and porewater composition before experiment start and 1 year after experiment running

Status before application of whey in Oct. 2007

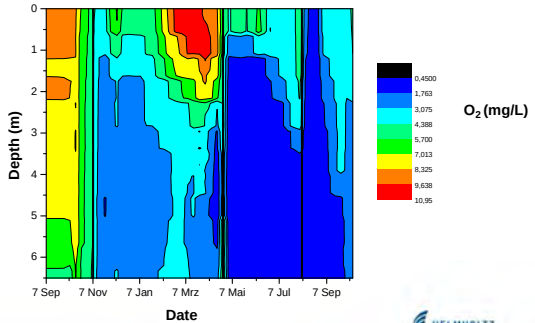
pH: **2.5 – 2.6**

O_2: **55% at bottom of enclosure**

Eh (in-situ): 450 mV at bottom of enclosure

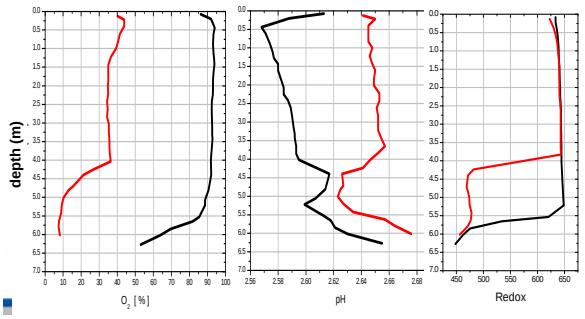


Oxygen in the water column of LE-8

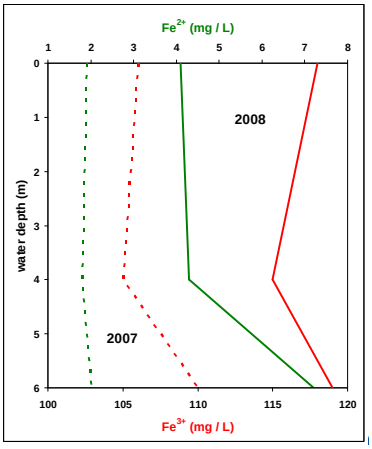


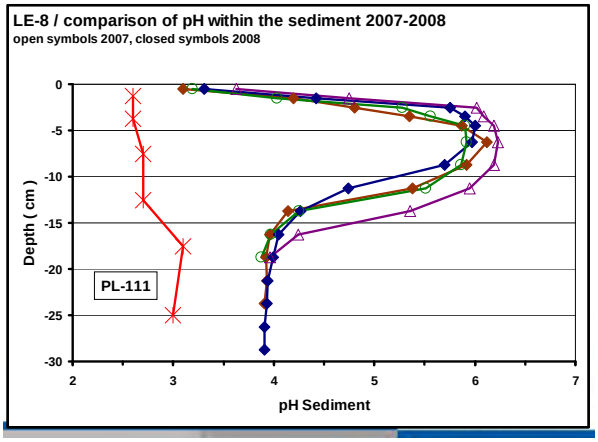
Oxygen concentration measured with Idronaut probe. The vertical lines indicate dosage of whey.

Physico-chemical profiles LE-8 black 2007 / red 2008

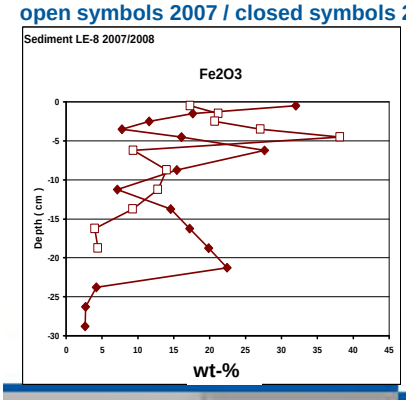


Iron within the water column of LE-8





Sediment
open symbols 2007 / closed symbols 2008



Sediment
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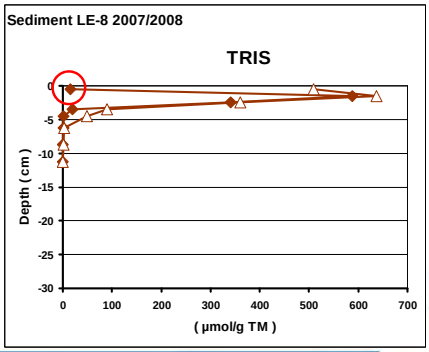
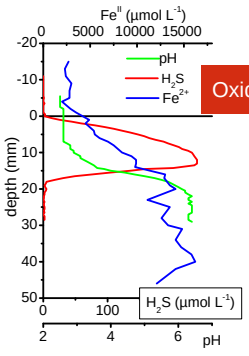
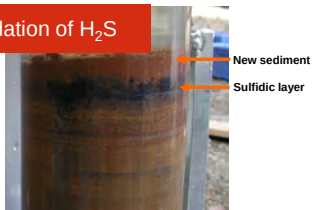


Vertical microprofiles



Oxidation of H_2S



- Fe(II) diffuses out of the sediment
- H_2S precipitates as sulfides at higher pH but diffuses out and is oxidised at low pH
- As the bottom water is anoxic, H_2S is obviously oxidised by Fe(III)

Summary

- **Consumption of O_2 in the water column**
- **Only small decrease of redox potential in the water**
- **No reduction of ferric iron to ferrous iron**
- **No change in pH-values within the water column and the sediment**
- **Increase** in **total iron** concentration in the **top cm** (*2)
- **No precipitation and accumulation of TRIS on the top layer of the sediment**

Conclusions

1. Is it possible to generate an anoxic water column within an enclosure and to maintain the anoxic conditions ?
   - Yes, by application of whey and **continuous** re-application; after Oct. 2008 no new application of whey
2. Is it possible to reduce all ferric iron within the water in this way ?
   - **No, the anoxic conditions reached were not sufficient**
3. Will the rate of neutralisation and the stability of the secondary sulfides be increased under the anoxic water conditions ?
   - **Unfortunately, not because of re-oxidation of secondary Fe-sulfides and H_2S by ferric iron**