



## Particulate matter as scavenger and carrier of trace metals in simulated mine water

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The brown and red colours of sulphidic mine waste and ore residues, as well as,,



...of the leachates, are visible evidences of the progressing weathering of iron sulphides...



...and precipitation of solid iron phases somewhere in the near-field or far-field



### Iron phases - secondary trace metal sources?

The secondary iron phases accumulate a substantial fraction of the trace elements originating from the sulphides (Cu, Zn, Cd, Pb, As etc)

#### QUESTION:

*What is the role of iron?*

*Iron, when present as a major metal component in the sulphides, and consequently in the leachates, largely determines how the other metals are transported, and eventually immobilized in sediments ?*



### Objectives

- Studies of the distribution of Cu, Zn, Pb and As between the solution and the solid colloidal iron phase that is generated when a water with these elements at low concentrations is mixed with a water with a high level of dissolved iron (mg/l level) that is allowed to precipitate
- Studies of the effects of humic acids, as well as of the presence of a consolidated particle phase (gibbsite) in the water, on the trace element distribution in the presence of iron

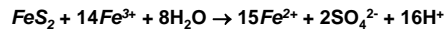
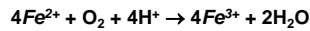
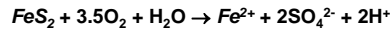


### Iron sulphides - the iron sources

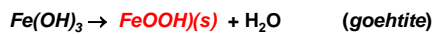
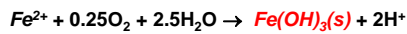
Pyrite	FeS <sub>2</sub>
Pyrrhotite	FeS
Arsenopyrite	FeAsS
Chalcopyrite	Cu FeS <sub>2</sub>
....	...



### Sulphide oxidation

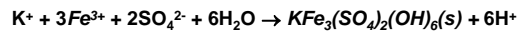


### Oxidation/precipitation

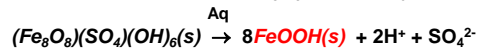
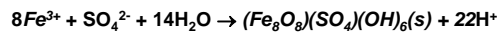


### Hydroxy sulphate phases

Jarosite (pH<2.5)



Schwertmannite (pH 2.8-3.2)



### Solid iron phases, mainly schwertmannite



### Experimental

Waters were prepared:

- One "Groundwater" with dissolved iron
- Three "Surface waters" + with additives (precipitating iron, humic acid)
- Four "River waters" with trace metals + additives (gibbsite particles, humic acid)





### Test waters

"River waters": Stock +

- *TM* (C) only trace metals
- *TM* + *Part* (P) trace metals + gibbsite
- *TM* + *HA* (HA) trace metals + humic acid (org)
- *TM* + *Part* + *HA* (M) trace metals + gibbsite and org.

"Groundwater": Stock +

- *Fe*, anaerobic (G) only iron (red)

"Surface waters": Stock +

- --- (C) only salt background
- *Fe*, aerated (O) only iron (ox; particles)
- *Fe* + *HA* (S) iron + org.



### Test waters

Stock solution:

- 0.1 mM NaHCO<sub>3</sub> + 0.1 mM CaSO<sub>4</sub>, pH 6  
(Na 2.3 mg/l, Ca 4 mg/l, HCO<sub>3</sub> 6.1 mg/l, SO<sub>4</sub> 9.6 mg/l)

Trace metals (*TM*):

- Cu 100 µg/l, Zn 500 µg/l, Pb 10 µg/l, As 5 µg/l,

Additives:

- Gibbsite 0.5 mg/l (0.063-0.125 mm) (*Part*)
- Fe(II) 2 mg/l (*Fe*)
- Na-humic acid 12 mg/l TOC (*HA*)



### Procedure

Each "River water" was mixed with an equal volume of each "Surface water" and the "Groundwater" giving 16 combinations:

- All 16 with trace metals
- 8 with added gibbsite particles
- 12 with added iron
- 10 with added humic acid



### Sampling and analysis

Samples were taken from the 16 water mixtures after 1, 5, 24 and 48 h.

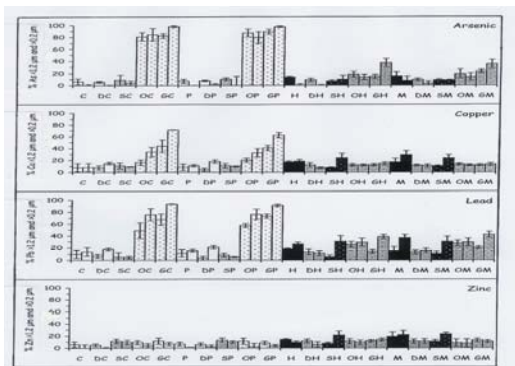
3 fractions were withdrawn:

- (1) Agitated, with its load of suspended particles
- (2) Filtered, through a 1.2 µm-filter, and
- (3) Filtered, through a 0.2 µm-filter  
(Micro Filtration system, polypropylene equipment; Millipore polycarbonate filters).

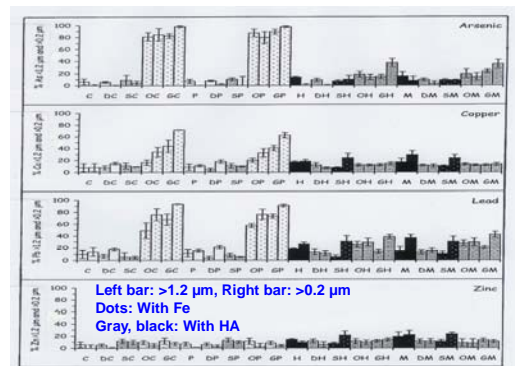
Metal analysis by ICP-MS



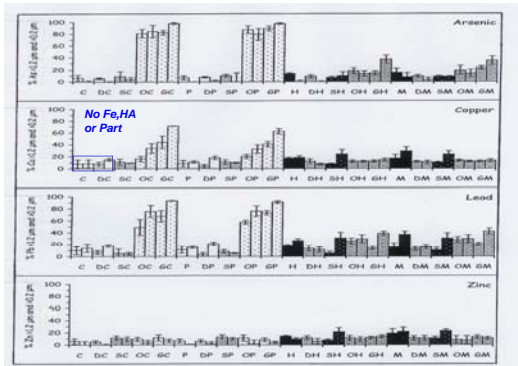
Percent of T.E. in the particle fraction (>1.2 µm, >0.2 µm)



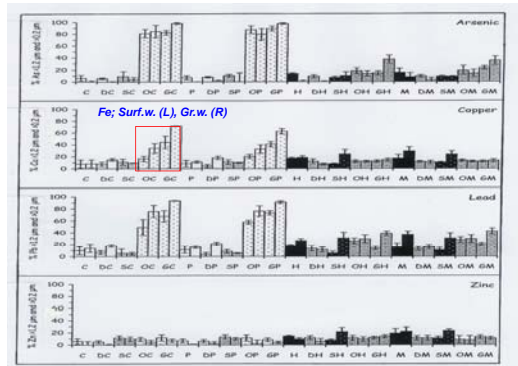
Percent of T.E. in the particle fraction (>1.2 µm, >0.2 µm)



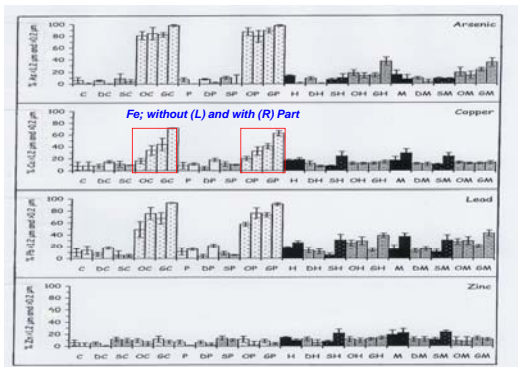
Percent of T.E. in the particle fraction (>1.2 μm, >0.2 μm)



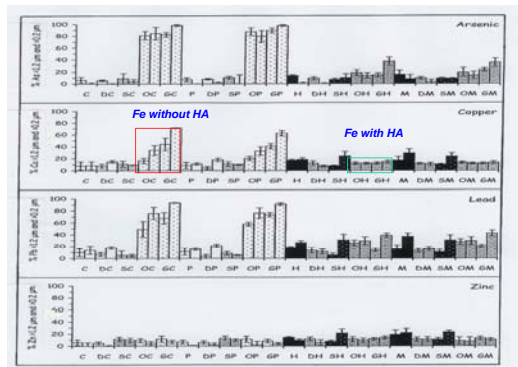
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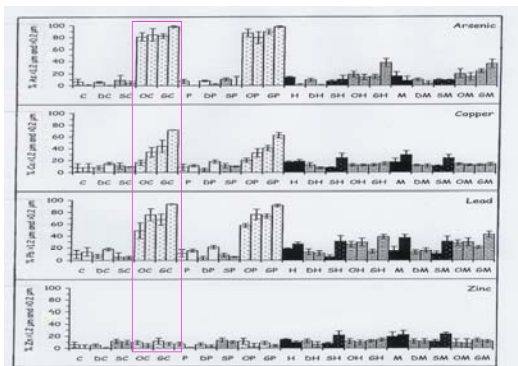
Percent of T.E. in the particle fraction (>1.2 μm, >0.2 μm)



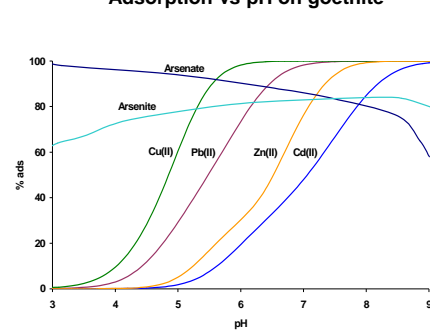
Percent of T.E. in the particle fraction (>1.2 μm, >0.2 μm)



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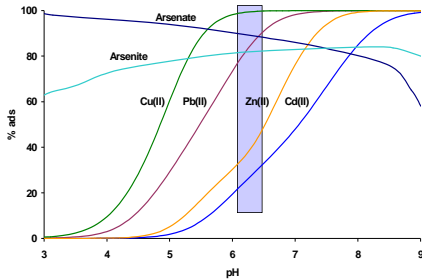


Adsorption vs pH on goethite





### Adsorption vs pH on goethite



### Summary and conclusions

- The total concentrations of all constituents in the various water mixtures reflected the composition of the original waters, however with minor losses of Fe, Cu, Pb and As with time (adsorption on vessel walls?).
- The partition of iron and the trace elements between the two suspended size fractions and solution were largely established and constant already after 1 h (pH 6-6.5)



### Summary and conclusions

- Even minor amounts of Fe-oxyhydroxides can act as efficient scavengers of dissolved trace elements at near neutral pH. (71% of Cu, 94% of Pb and 99% of As in the particles >0.2 µm after 1 h).
- Humic acids will significantly reduced the trace element uptake on the Fe-precipitate
- Fresh precipitates of Fe are by far more efficient trace element carriers than consolidated particles (gibbsite) already present in the water



### Comments

Aspects to consider in a performance assessment of a particular site or case:

- How fast is the sulphide oxidation - by air, as well as by Fe(III) (vs pH) ? Can the oxidation of sulphides proceed at high pH in the absence of air ?
- Role of microbes - determine the rate (but not thermodynamics)
- What is the carrying capacity of precipitates with respect to the trace metals - co-precipitation and adsorption of trace metals (vs pH) ?



### Comments

- The iron may largely determine the transport and subsequent accumulation of trace metals!

Where is Fe(II) eventually oxidized and precipitated as a solid Fe(III) hydroxy phase?



### Acknowledgements

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Oxidation (by air) governed by microbial processes?

