Fractionation and leachability of Fe, Zn, Cu and Ni in the sludge from a sulphate-reducing bioreactor treating metal-bearing wastewater

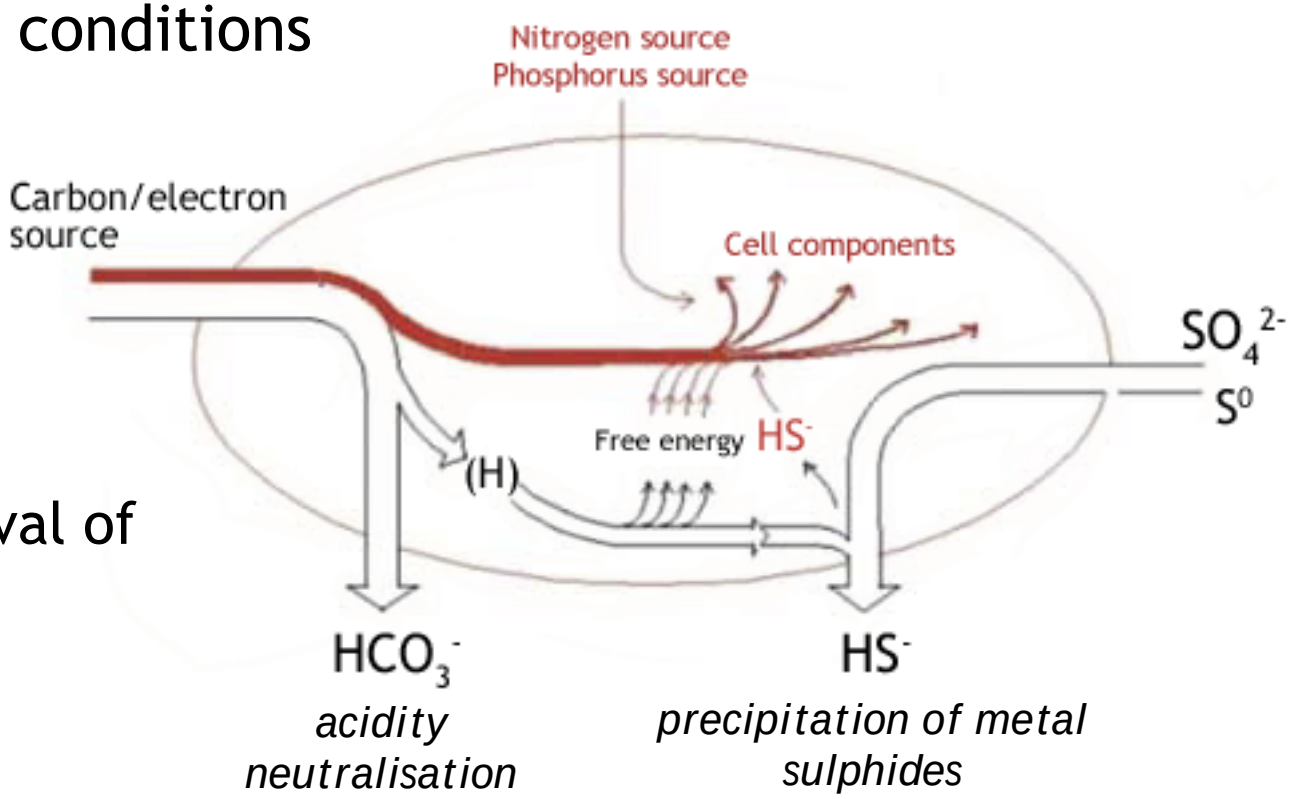
P. Kousi, E. Remoundaki, A. Hatzikioseyian, V. Korkovelou & M. Tsezos

Laboratory of Environmental Science and Engineering
School of Mining and Metallurgical Engineering
National Technical University of Athens (NTUA)

ATHENS 2017, 5th International Conference on Sustainable Solid Waste Management
21-24 June 2017, Athens, Greece

Process:
Microbially mediated sulphate reduction

- by sulphate-reducing bacteria (SRB)
- under anaerobic conditions



Process benefit:

simultaneous removal of
-sulphate
-metal ions
-acidity
-organic carbon

Metal ion sequestering – Sludge formation

Prevailing mechanism:
bioprecipitation of metal sulphides

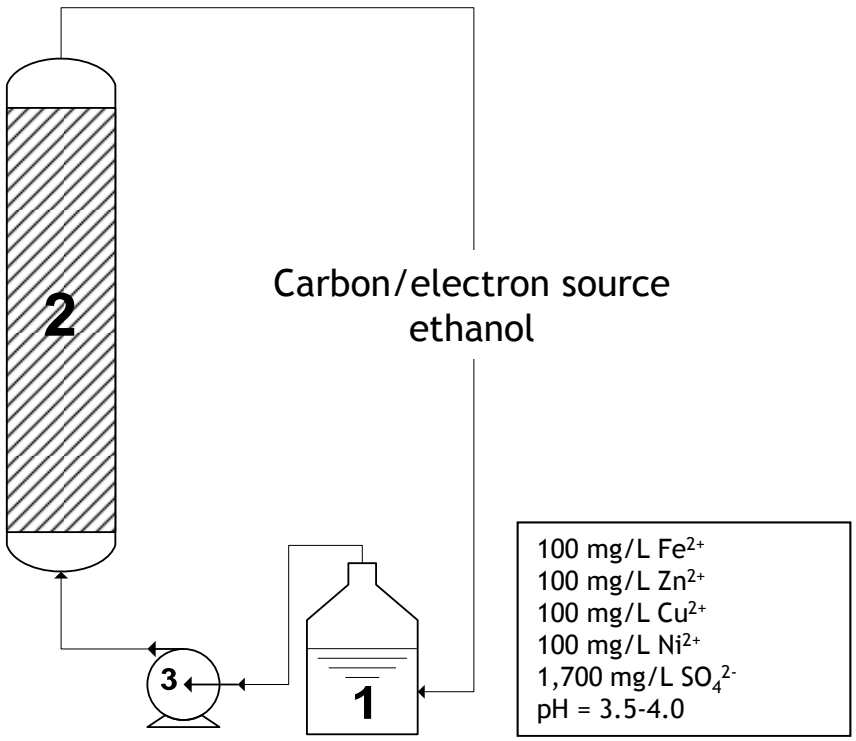
- A key aspect of the sustainability of the process, besides its effectiveness, is the **management of the generated sludge**
- Potential scenarios range from **disposal via landfilling** to further treatment for **metal recovery**

Bioreactor

Upflow, packed-bed reactor

Biofilm established on porous ceramic pipes 1 cm long

(Cermec®, JBL Germany)



1. Sulphate- and metal-bearing substrate solution
2. Sulphate-reducing bioreactor
3. Peristaltic pump

<u>Operation:</u> batch mode
for 6 years
at room temperature

Issue addressed:
Propose sludge management options for overall process sustainability

Relevant questions:

1. Is the sludge safe for disposal via landfilling?
2. Is the metal content of the sludge recoverable?

Issue addressed:
sludge management for overall process sustainability

Formation mechanism

- mineral phases

→ Sludge stability

Other factors (temp, pH, sulphide)

- crystallinity
- particle size

→ Metal mobility

Methodology

Sludge samples from the bottom of the reactor → *low redox and neutral pH conditions*

Physical, chemical, mineralogical characterisation

- Laser Diffraction – Low Angle Laser Light Scattering
- X-Ray Diffraction
- Thermogravimetry-Differential Scanning Calorimetry
- Scanning Electron Microscopy / Energy Dispersive X-ray Spectrometry

Methodology

Metal fractionation

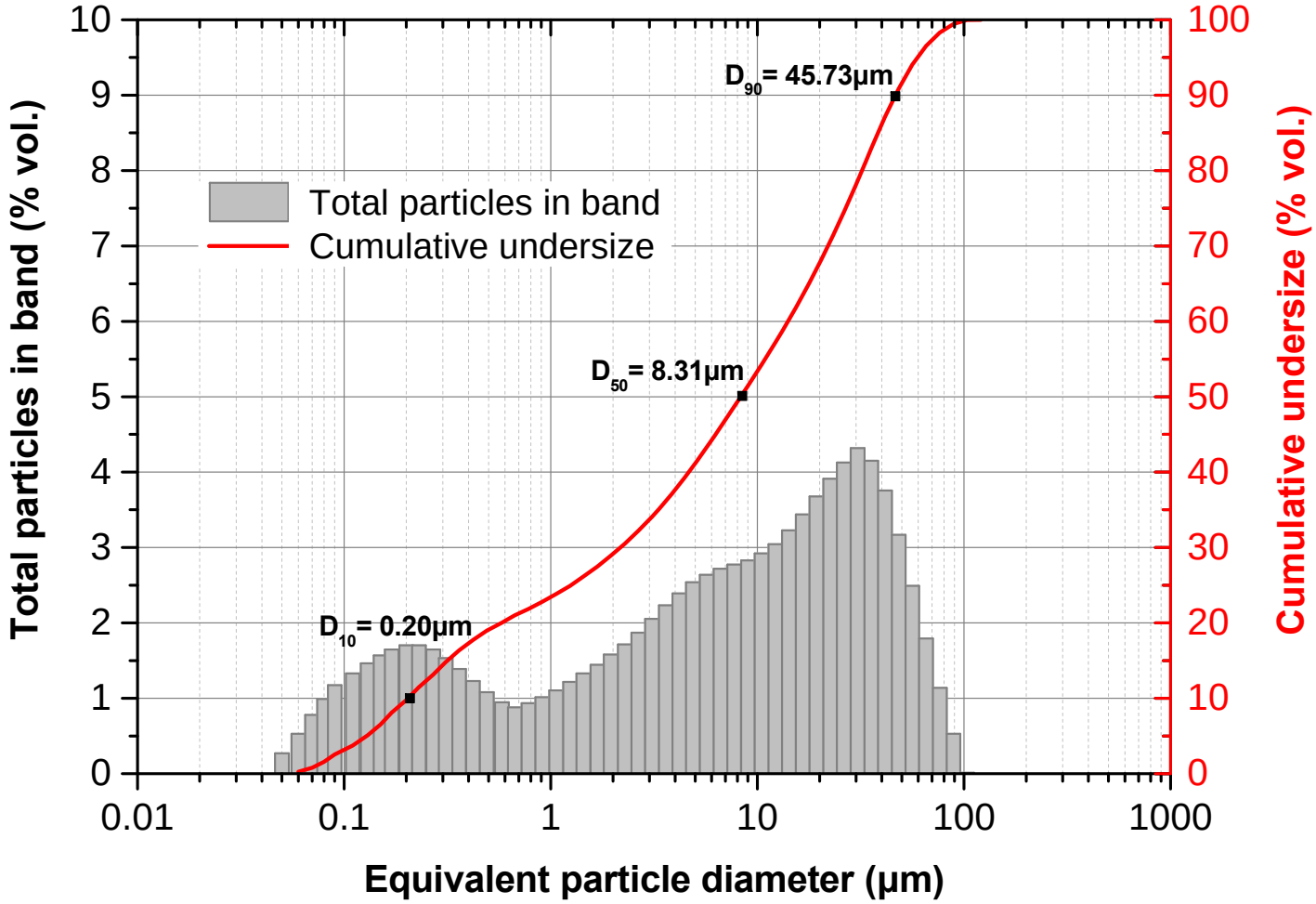
Sequential extraction method (Tessier)

Metal leachability and environmental stability

- EN 12457-2
- TCLP
- pH-time effect

RESULTS

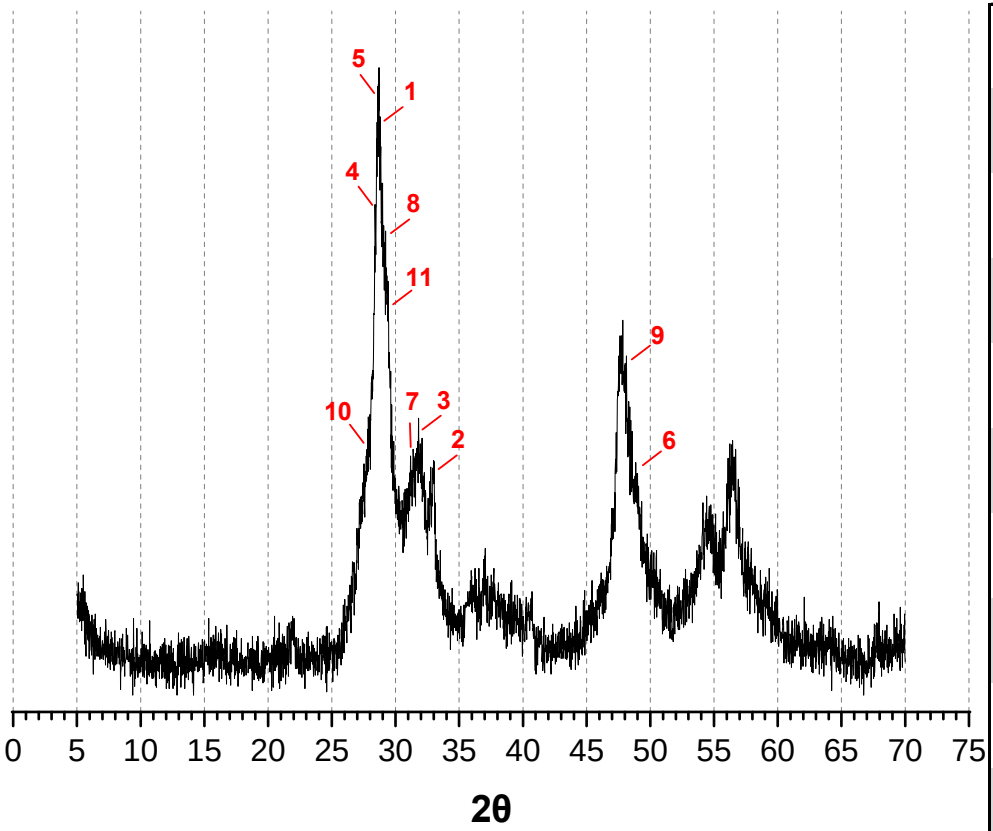
Particle size distribution



Sludge composition

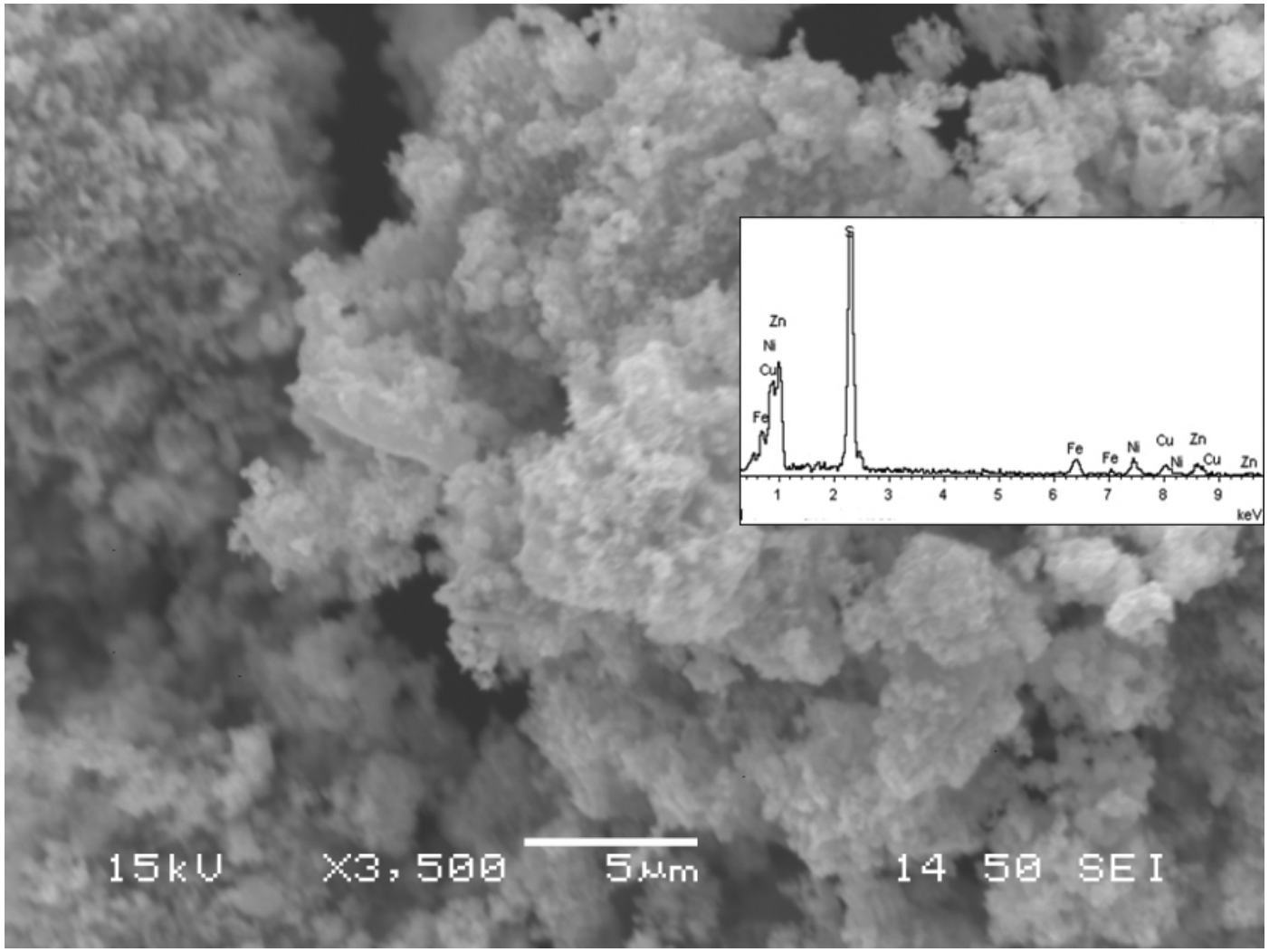
Parameter	Value (wt. %, dw)
Iron	14.80
Zinc	18.73
Copper	18.24
Nickel	17.71
Total metal content	69.48
Sulphur (total)	31.22
Carbon (total)	5.00
Volatile solids	14.70

Mineralogy - XRD

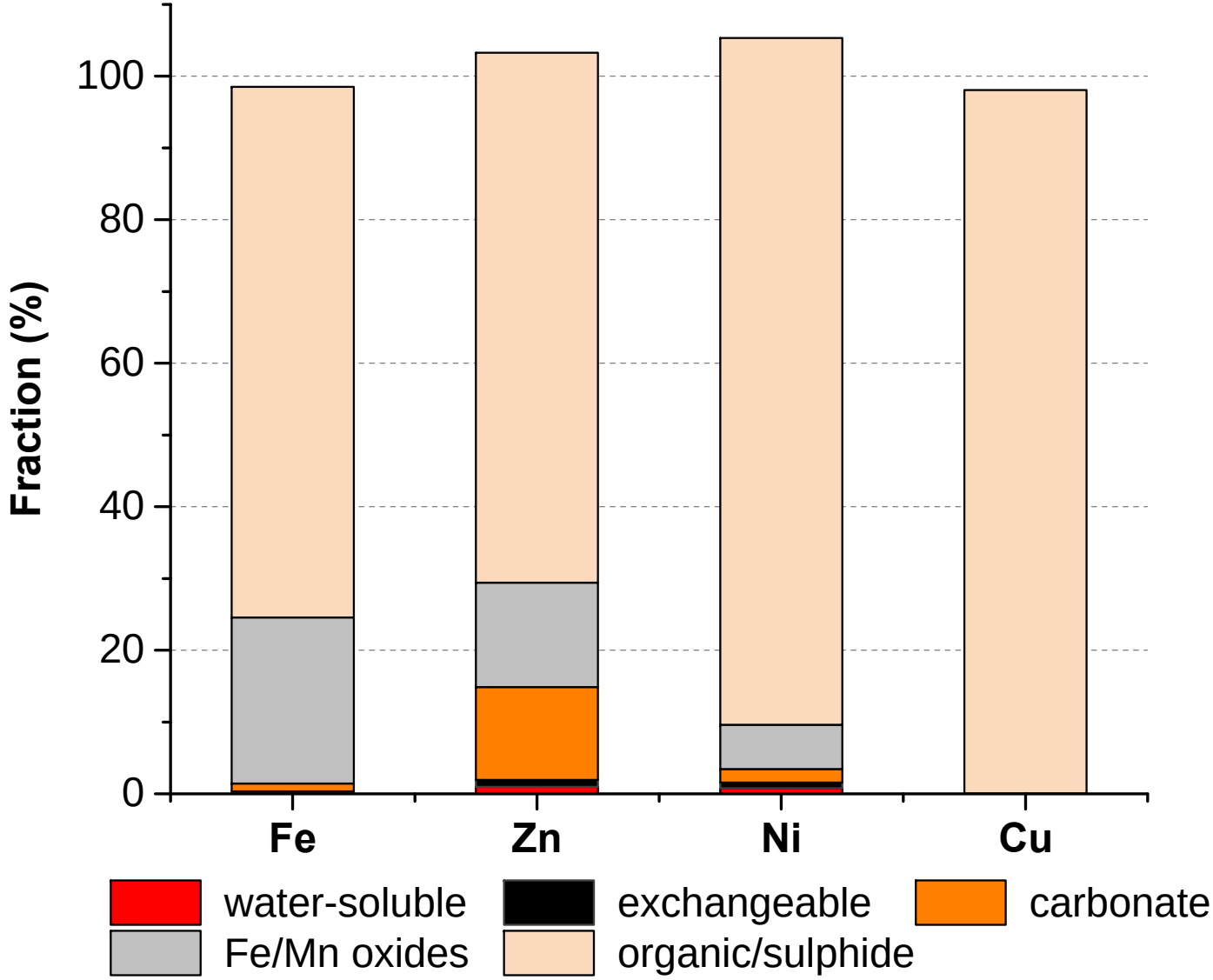


1	FeS_2	pyrite
2	$FeCO_3$	siderite
3	CuS	covellite
4	Zn_5S_5	wurtzite
5	ZnS	sphalerite
6	NiS	millerite
7	Ni_3S_2	heazlewoodite
8	$Cu_4Fe_5S_8$	haycockite
9	Cu_2FeS_2	bornite
10	$CuFe_2S_3$	cubanite
11	$CuFeS_2$	chalcopyrite

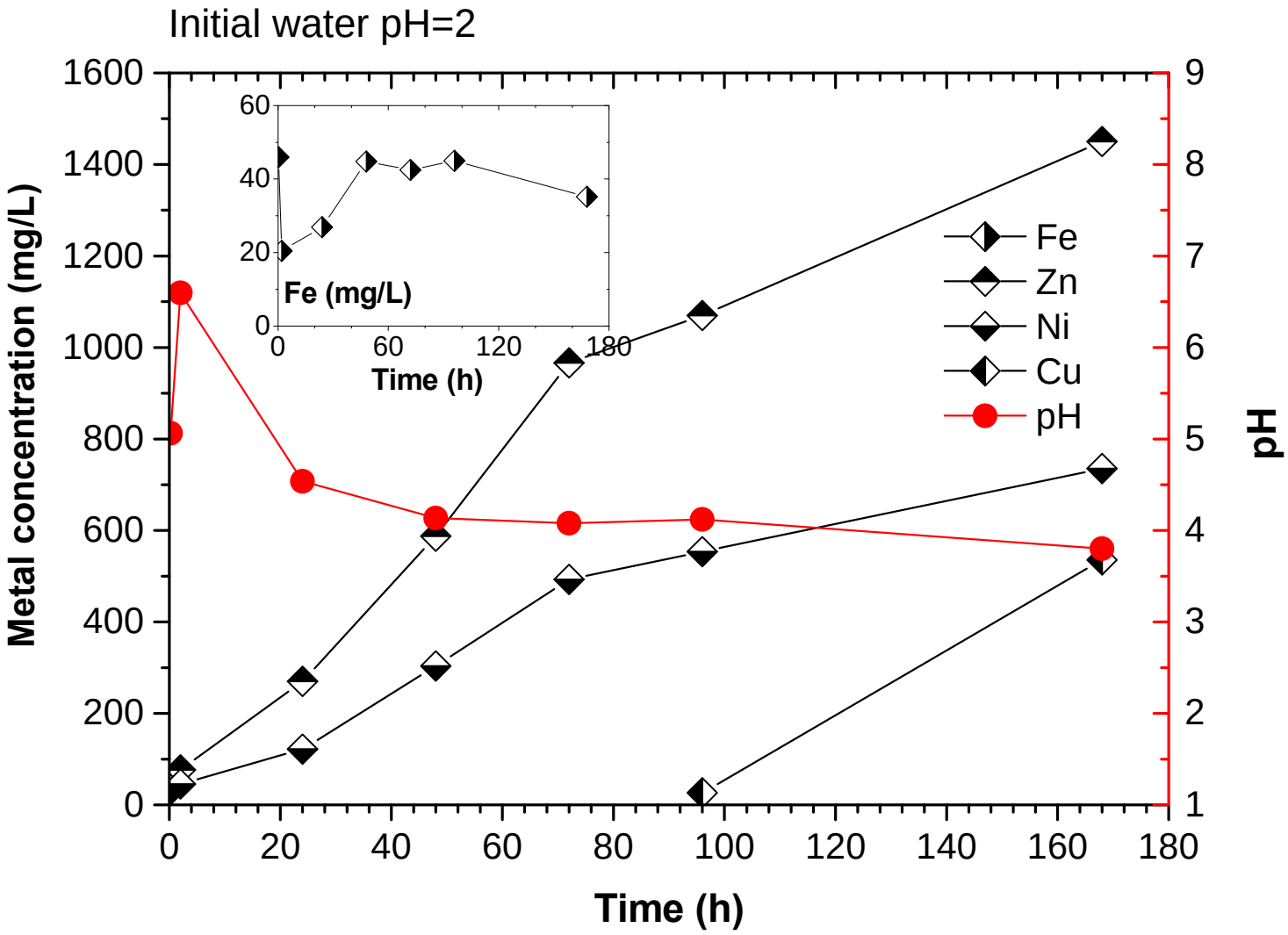
Mineralogy – SEM/EDS



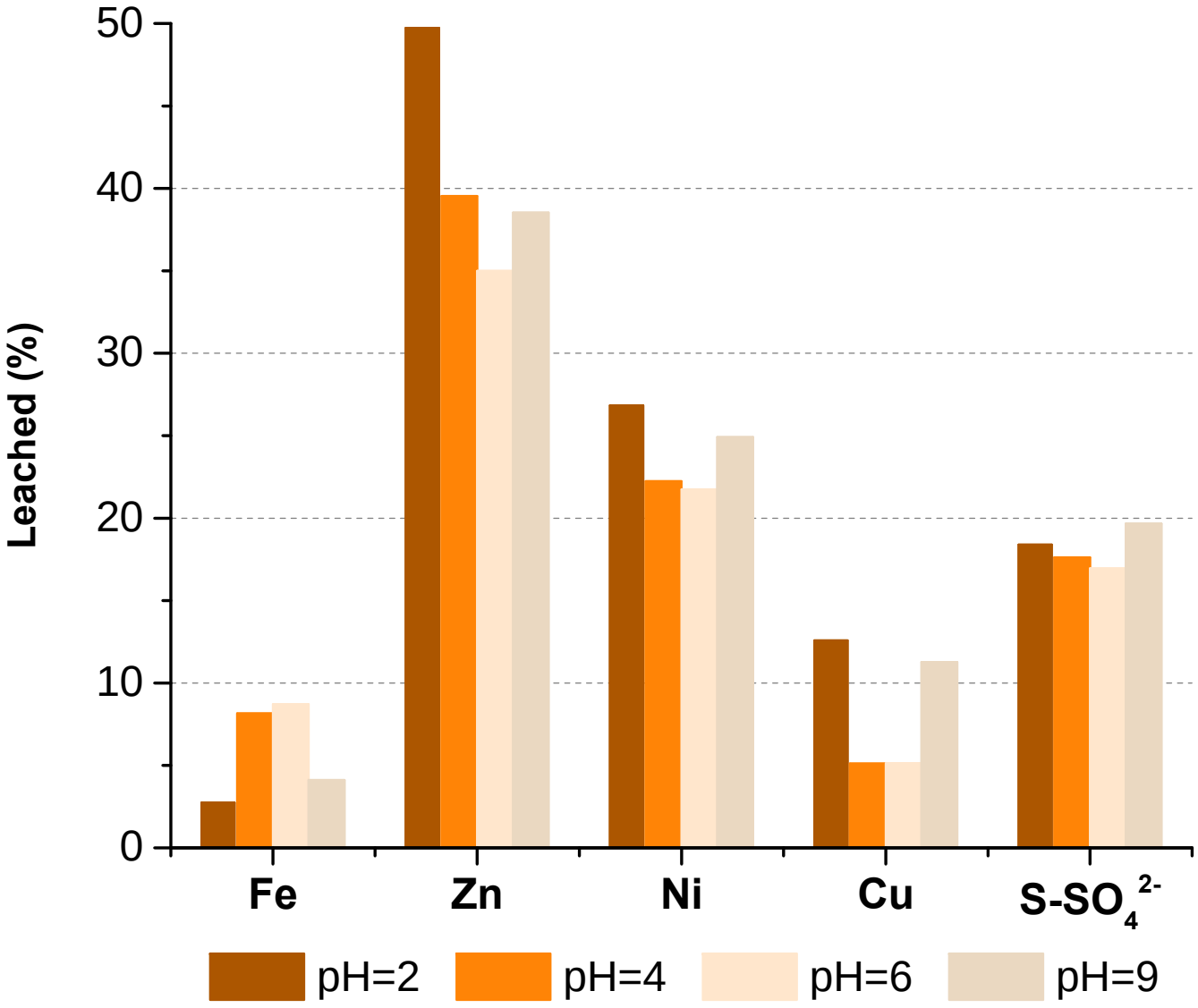
Metal fractionation



Environmental stability



Environmental stability (long-term)



Conclusions

- 90 % of the particles are smaller than 47 μm,
  50 % of the particles are smaller than 8.5 μm
- Amorphous or poorly crystalline phases and aggregates of Fe, Zn, Cu, Ni sulphides
- Metal content adds to 70 % dw:
  Fe (14.8 %), Zn (18.7 %), Ni (17.7 %), Cu (18.2 %)
- Main metal sulphides determined:
  pyrite, covellite, wurtzite/sphalerite and millerite/heazlewoodite

Conclusions

- The sludge is characterised as hazardous and inappropriate for disposal via landfilling without any prior treatment.
- The sludge fine grain size and poorly crystalline structure, as well as the direct oxidation of sulphide upon exposure to water/air, render the high metal content (70 % dw) of the sludge recoverable.

Relevant Publications

Remoundaki, E., Kousi, P., Joulian, C., Battaglia-Brunet, F., Hatzikioseyian, A., Tsezos, M.: Characterization, morphology and composition of biofilm and precipitates from a sulphate-reducing fixed-bed reactor. **J. Hazard. Mater**. 153(1-2), 514-524 (2008)

Kousi, P., Remoundaki, E., Hatzikioseyian, A., Battaglia-Brunet, F., Joulian, C., Kousteni, V., Tsezos, M.: Metal precipitation in an ethanol-fed, fixed-bed sulphate-reducing bioreactor. **J. Hazard. Mater**. 189, 677-684 (2011)

Kousi, P., Remoundaki, E., Hatzikioseyian, A., Tsezos, M.: Sulphate-reducing fixed-bed bioreactors fed with different organic substrates for metal precipitation. In: Qiu, G., Jiang, T., Qin, W., Liu, X., Yang, Y., Wang, H. (eds**.) Biohydrometallurgy: Biotech key to unlock mineral resources value**, Proceedings of the 19th International Biohydrometallurgy Symposium (IBS 2011), Changsha, China, 18-22 September 2011, pp. 1078-1084. Central South University Press (2011)