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Recovery of metals using biometallurgy

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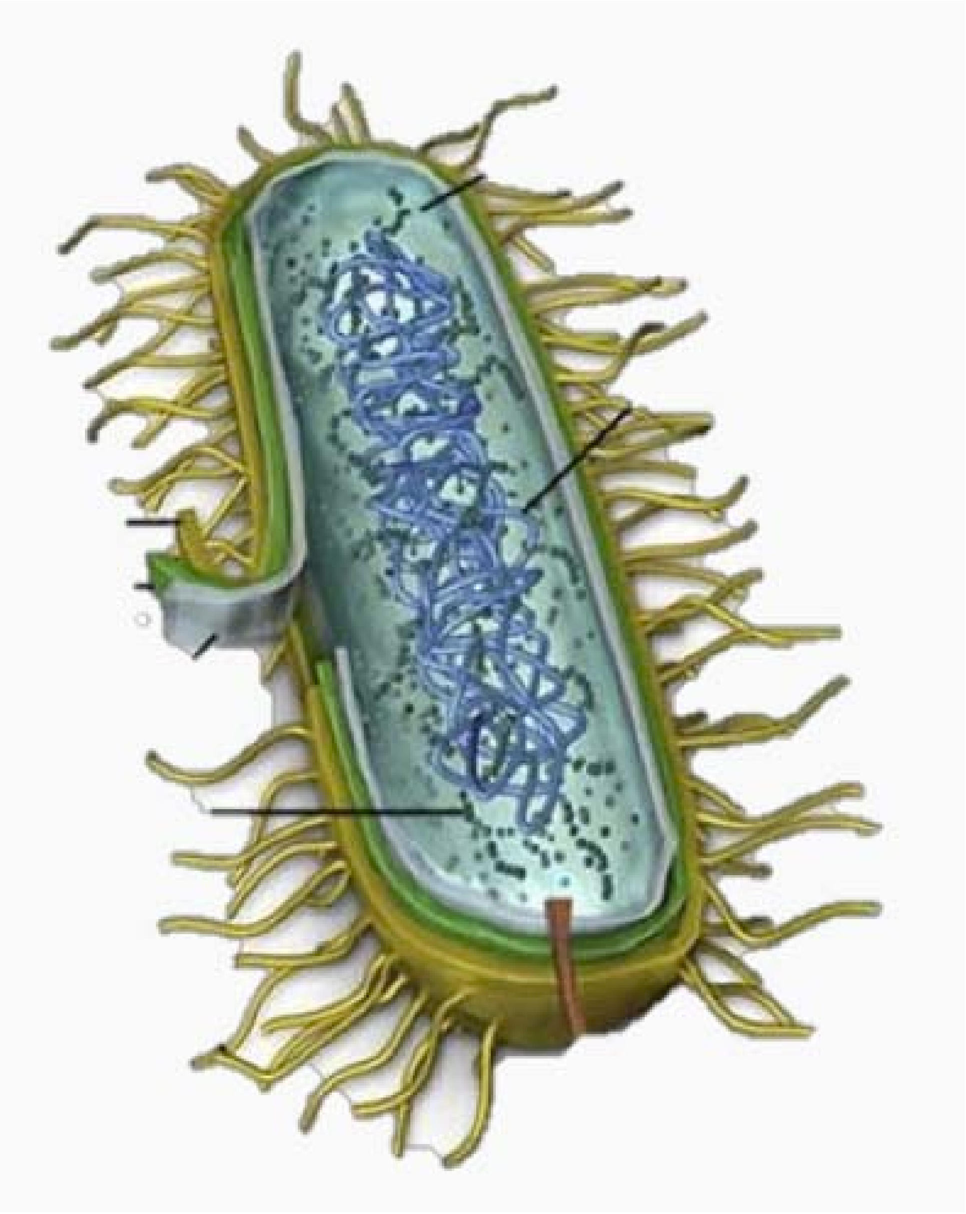
The evolutionary story



Bacteria

- 1 μ m sized prokaryotic organisms
- Essential in nutrient cycles of C, N, P and S
- Can live in extreme environments (T, P, pH, heavy metals)
- Pure or Mixed cultures / The latter can evolve to become “microbiomes“
- They do it for a living! Either get electrons from the metal or deposit electrons on the metal

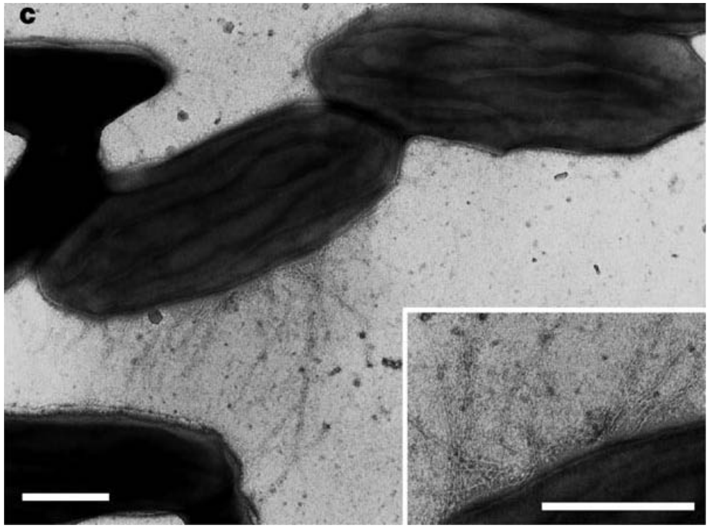
Bacteria

- Gibbs free energy
  - $Pd^{2+} + 2\ e^- \rightarrow Pd(0)$ $\Delta G = -88.3$ kJ/electron
  - $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\Delta G = -74.4$ kJ/electron

  - $Fe(s) \rightarrow Fe^{2+} + 2\ e^-$ $\Delta G = -91.5$ kJ/electron

Biometallurgy

- Based on the interactions of living organisms with metals
- Special focus on bacteria
  - Certain species have high affinity for metals (cf *Shewanella*, *Geobacter*): they interact with the metals with special cytochromes/siderophores or even nanowires



Reguera et al., *Nature*, 2005, 435: 1098-1101

Biometallurgy

- Complex metabolic and physiochemical interactions possible
  - Sorption
  - Reduction/Oxidation
  - Complexation
  - Precipitation
  - Leaching

Biotechnology in mining

- **Open system**

Biotechnology in mining

- **Reactor system**
- Bacteria-metal interactions already applied on full scale in mining: bioleaching of Cu/Fe/Au
- South-Africa, Mexico and Chile

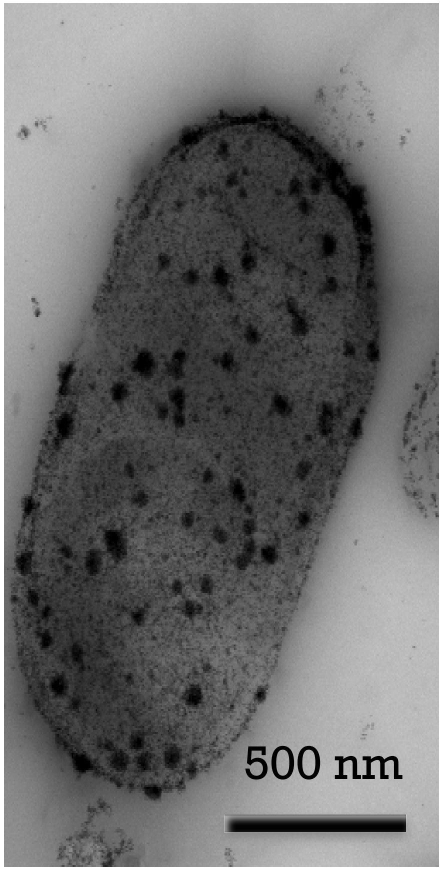
Biotechnology in mining

- Annual world production of Cu, Co, Au, Ni, U and Zn by bioleaching amounted to **3.6 million tonnes** in 2000

- Actually, bioleaching generates **25 to 30 %** of the world's copper production
  (Brierley, *Trans Nonferrous Met Soc China*, 2008, 18: 1302-1310)

New insights

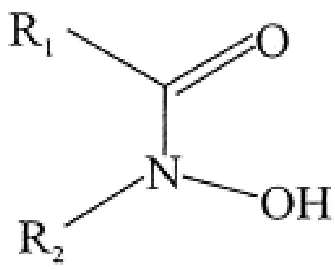
Bacteria-metal interactions



Processes

1. Solubilisation/Sorption

- High specific surface area (> 100 m^2/g living biomass)
- Presence of functional groups on external structures



Hydroxamate

- Can grow in complex 3-dimensional structures, e.g. biofilms and granules
  - Presence of biopolymers provides more available sorption sites
- As yet, little or no application in an industrial context

Processes

2. Reduction

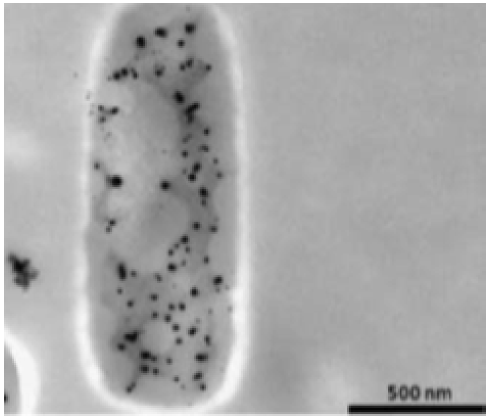
- Preceeded by sorption of ionic metal or metal complex on the cell wall
- Formation of extracellular, intracellular or periplasmic zerovalent metal nanoparticles
- Reduction process:
  - Enzymatically: metals as final electron acceptor (e.g. Bio-Pd)
  - Chemically: reducing structures on the bacterial cell wall (e.g. Bio-Ag)
- Mainly described for Ag, Au and Pd

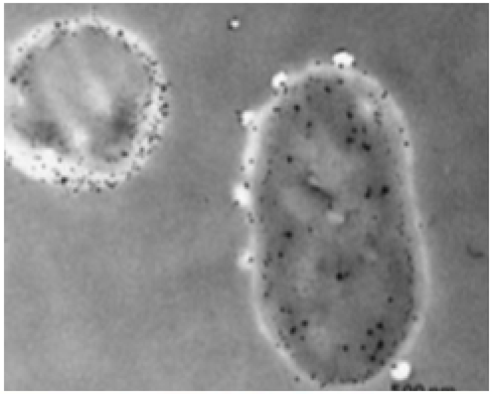
Processes

Bio-Ag

- Non-enzymatic production of silver nanoparticles
- *Lactobacillus* spp. used for rapid and efficient bio-Ag production

(Sintubin et al., *Appl Microbiol Biotechnol*, 2009, 84: 741-749; LabMET)

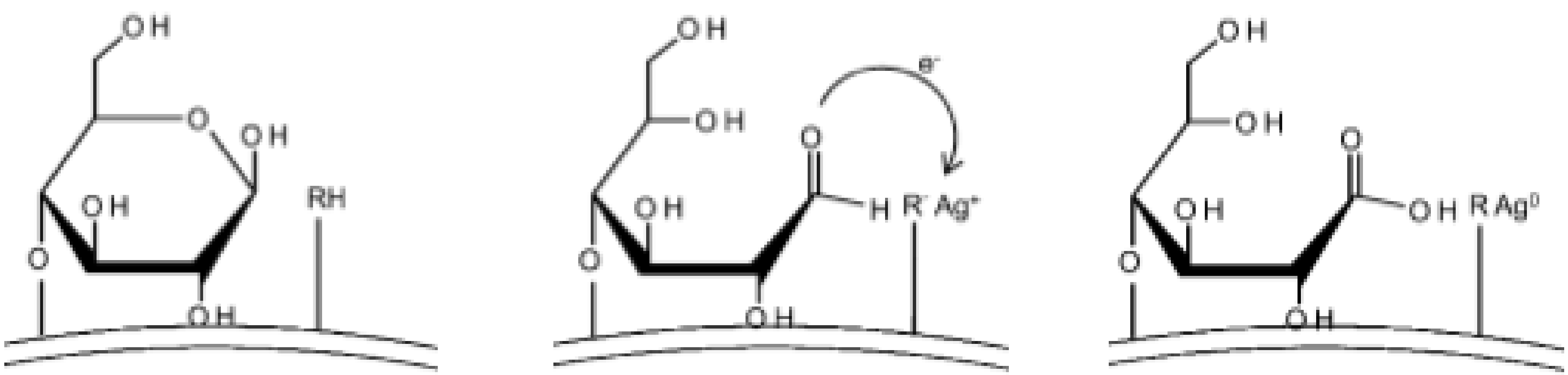




Processes

Bio-Ag

- Mechanism: reducing sugars at the cell surface function as the electron donor in the reduction of Ag^+ to its metallic form Ag^0
- pH dependent proces: high pH catalyzes ring opening



Processes

Bio-Ag: Applications

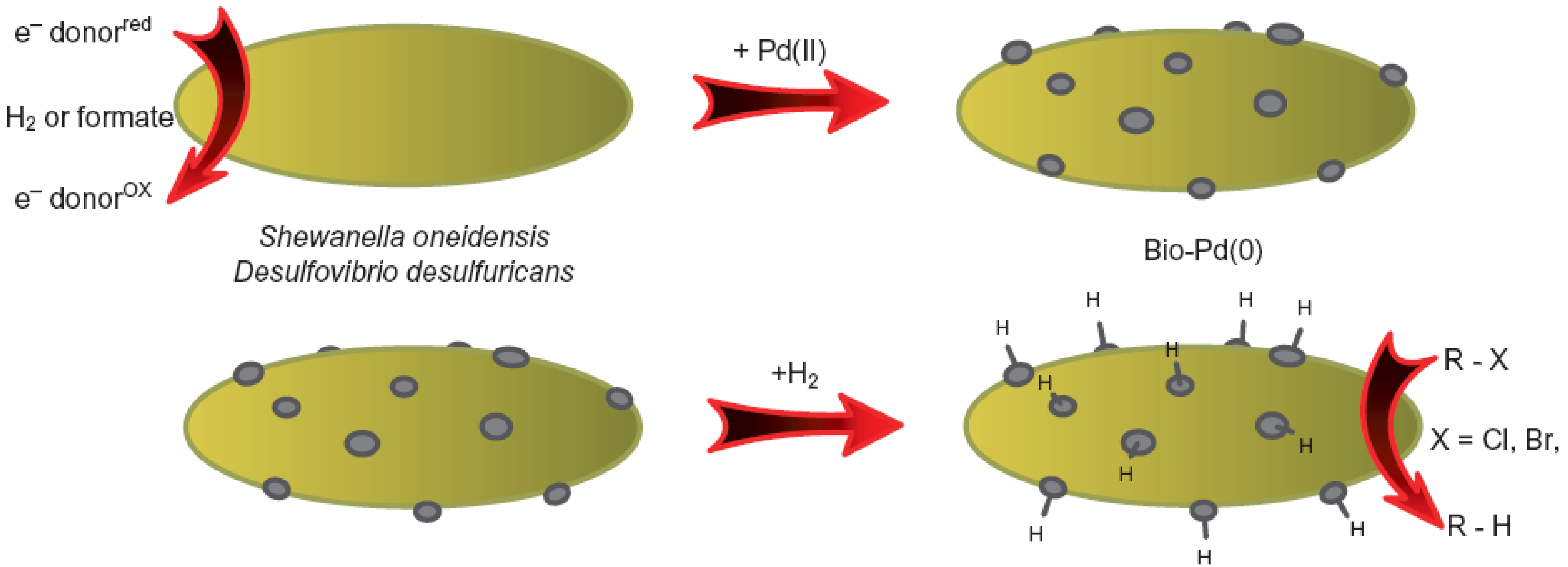
- Strong antimicrobial properties. Silver nanoparticles are applied in a large variety of applications to control microbial growth
  (Sintubin et al., *Appl Microbial Biotechnol*, 2011, 91: 153-162; LabMET)

- Use as disinfectant for the removal of viruses out of drinking water
  (De Gusseme et al., *Appl Environ Microbiol*, 2010, 76: 1082-1087; LabMET)
  (De Gusseme et al., *Water Res*, 2011, 45: 1856-1864; LabMET)

(Sintubin et al., *Biotechnol Bioeng*, 2012, 109: 2422-2436; LabMET)

Processes

Bio-Pd



(De Corte et al., *Microbial biotechnology*, 2011, 5: 5-17; LabMET)

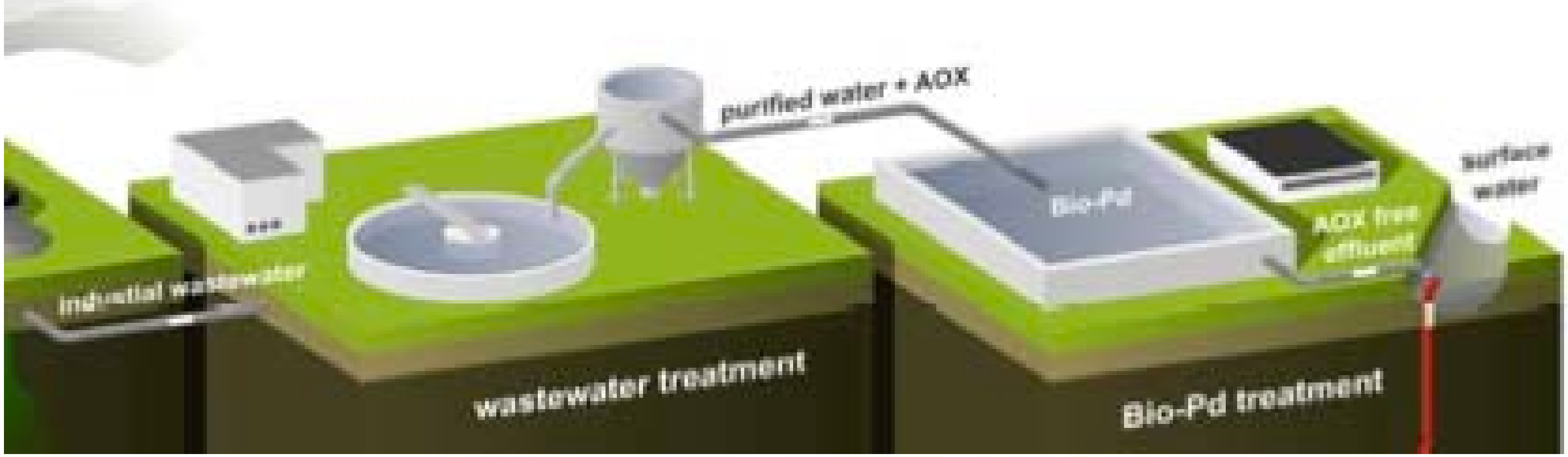
Processes

Bio-Pd: Applications

- Catalyst for dehalogenation of environmental contaminants

  Effluent polishing techniques

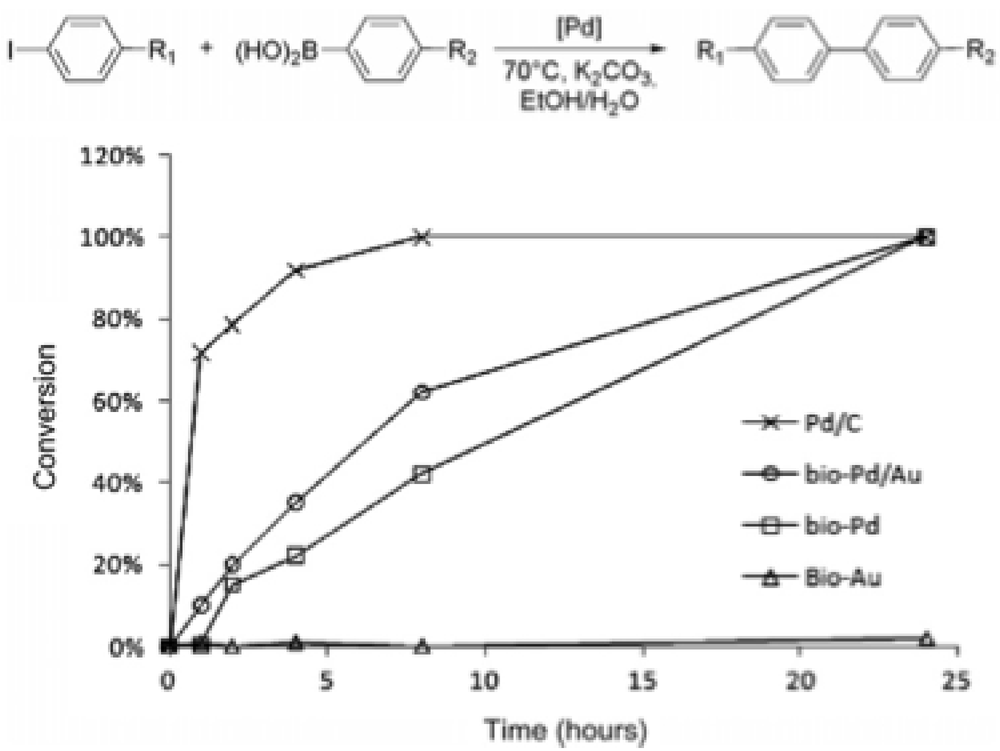
(Hennebel et al., *Current Opinion in Biotechnology*, 2012, 23: 1-7; LabMET)



Processes

Bio-Pd: Applications

- C-C coupling reactions in chemistry

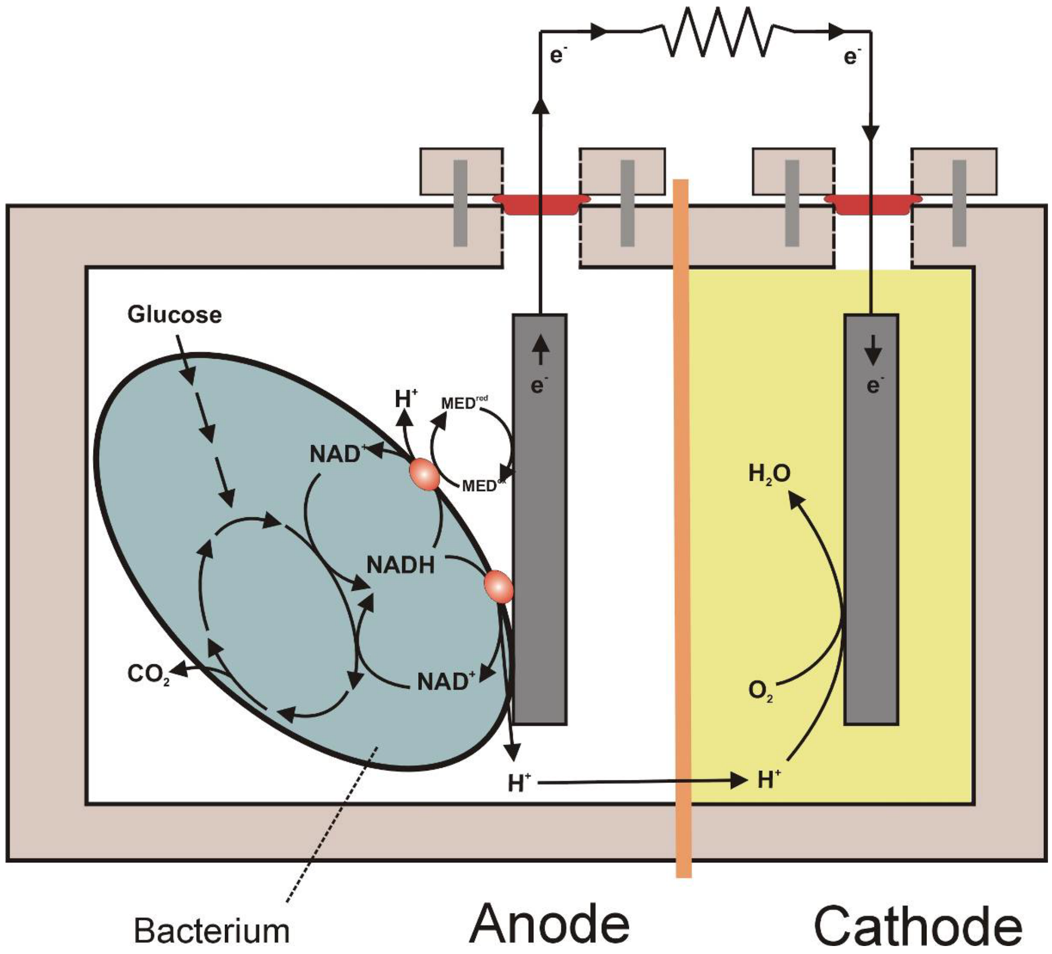


- Suzuki coupling reaction
- Bio-Pd/Au shows increased reaction rate

(Heugebaert et al., *Tetrahedron Letters*, 2012, 53: 1410-1412; LabMET)

Processes

3. Bioelectrochemical metal conversions



(RABAEY et al., 2005. Trends in biotechnology 23: 291-298; LabMET)

(RABAEY et al., 2005. Environ. Sci. & Technol. 39: 3401-3408; LabMET)

+ Processes

3. Bioelectrochemical metal recovery

- Microorganisms can catalyze electrode

 reactions

-Opportunities

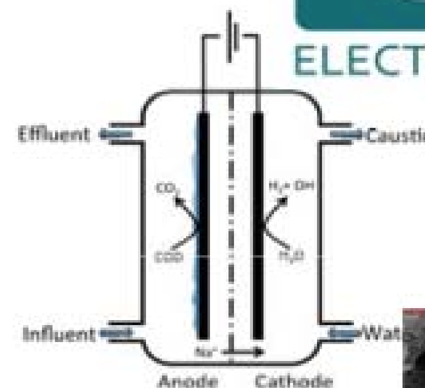
- Direct metal oxidation/reduction
- Cathodic in situ sulphide production for
  metals precipitation

-Examples

*Cathodic gypsum transformations

*Advanced bioleaching eg by H2O2
 production at cathode

ELECTROTALK



Supported by ERC ELECTROTALK, EU-FP7, …

(Rabaey et al., *Environ Sci Techol*, 2010, 44: 4315-4321; LabMET)

Processes

4. Other transformations

- **Oxidation**: e.g. formation of biogenic MnO_2
  (Forrez et al., *Environ Sci Technol*, 2010, 44: 3449-3454; LabMET)

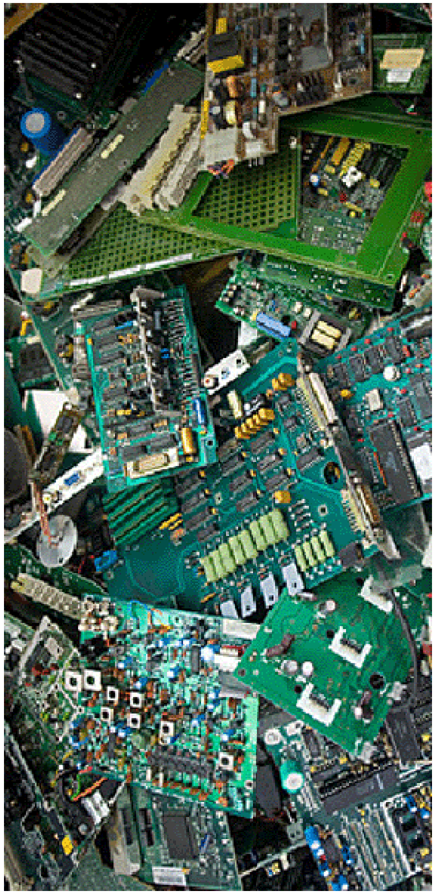
- **Precipitation as sulphides**: sulphate reducing bacteria reduce sulphate (SO_4^{2-}) to sulphide (S^{2-}), resulting in insoluble sulphides
  (Yoon et al., *Geoch Cosmoch Acta*, 2012, 84: 165-176)

- **Methylation** of Hg, Te, As, Sb and Se
  (Meyer et al., *Syst Appl Microbiol*, 2007, 30: 229-238)

- **Association with phosphates**
  (Rhee et al., *Current Biology*, 2012, 22: 237-241)

Potential biometallurgical applications

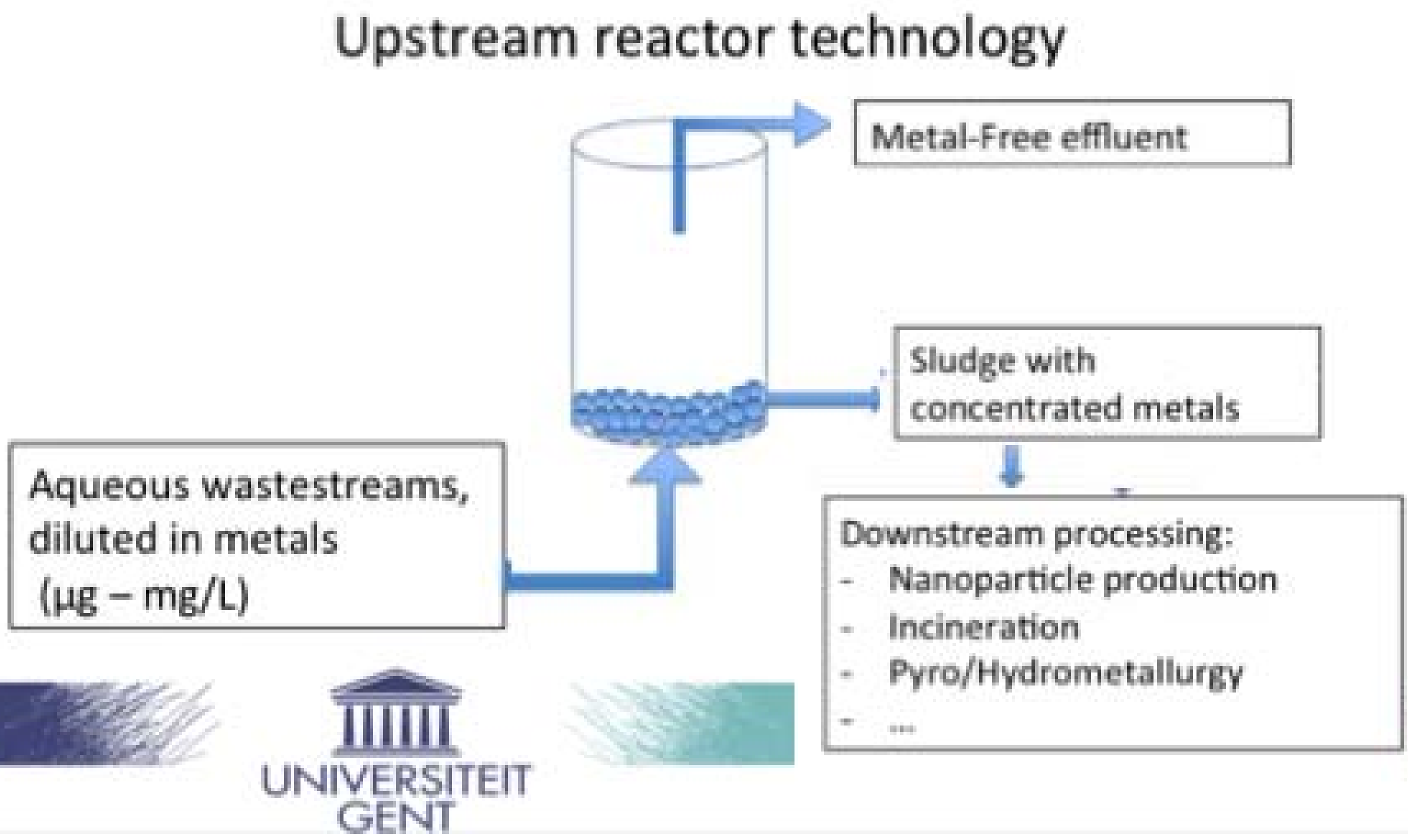
for recovery of critical metals



Potential biometallurgical applications

Aqueous waste streams

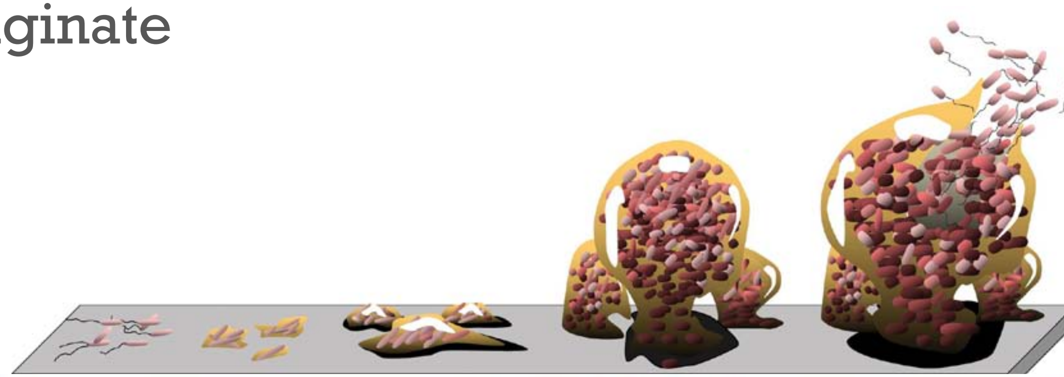
- Granulated bacteria for upconcentration of metals, present at very low concentrations (µg – mg/L) in industrial streams



Potential biometallurgical applications

Aqueous waste streams

- Application of bacteria possible under different forms
  - Free suspended cells
  - More complex structures: granules and biofilms/ microbiomes
  - They can be re-enforced by addition of biopolymers like chitosan or alginate



Potential biometallurgical applications

Aqueous waste streams

- Advantages of biometallurgy
  - No solvents or aggressive and toxic chemicals required or generated
  - Low amounts of energy required
  - Bacteria are renewable sorbents and reductants

Treatment of waste streams with low concentrations of critical metals is possible

+ Potential biometallurgical applications

Aqueous waste streams

Aqueous stream	Critical metals present	Concentration	Challenges
Hospital waste water	Pt, Gd	μ g/L	Extremely low concentrations
Waste water from PGM processing industry	PGMs	Few mg/L	Aggressive streams, different metal speciations, Interfering compounds
Washing liquid from used LCD panels	In, Ga	μ g - mg/L	Residues of Hg present
Others, to be identified	All	μ g - mg/L	Characterisation of streams urgently needed

(Lenz et al., *Chemosphere*, 2007, 69: 1765-1774)
(Gauthier et al., *Chemsuchem*, 2010, 3: 1036-1039)
(Mabbett et al., *Environ Sci Technol*, 2006, 40: 1015-1021)

Potential biometallurgical applications

Downstream processing

- Metals sorbed on biomass organic matter: Concentration ranges from 50 mg La/g dry matter of Pseudomonas; up to 500 mg Cd/g dry matter of granular microbial biomas
  (Texier et al., *Chemosphere*, 2002, 47: 333-342;
  Mabbett et al., *Environ Sci Technol*, 2006, 40: 1015-1021)

  Subsequent processing by conventional hydro-, pyro- or electrometallurgical processes

- Applying biogenic nanoparticles as a green catalyst for eg dehalogenation processes

Potential biometallurgical applications

Solid waste streams: bioleaching

- Most widely applied biometallurgical concept
- Based on transformation of minerals through microbial oxidation of iron and sulphur
- The exergonic processes dissolve Fe^{2+} and Cu^{2+} and permit microbial growth

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

$$CuS + 8\ Fe^{3+} + 4\ H_2O \rightarrow Cu^{2+} + 8\ Fe^{2+} + SO_4^{2-} + 8\ H^+$$

Potential biometallurgical applications

Solid waste streams: advantages of bioleaching

Compared to chemical leaching processes

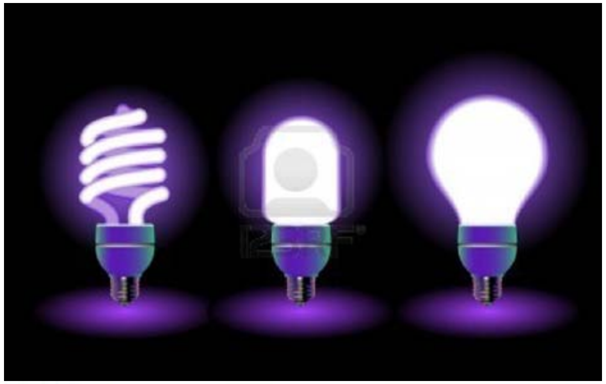
- Assumed to be economically competitive
  (Cui et al., *Journal of Hazardous Materials*, 2008, 158: 228-256)
- Lower requirements in energy consumption
- Pollution and waste generation is less
- Required acids are produced locally from harmless sources of sulphur

Potential biometallurgical applications

Solid waste streams: recovery of critical metals

Application of the mechanism of bioleaching for

- End-of-Life fluorescent lamps: lamp powder contains REEs europium, terbium and yttrium (Öko-Institut, 2012, Recycling critical raw materials from waste electronic equipment)

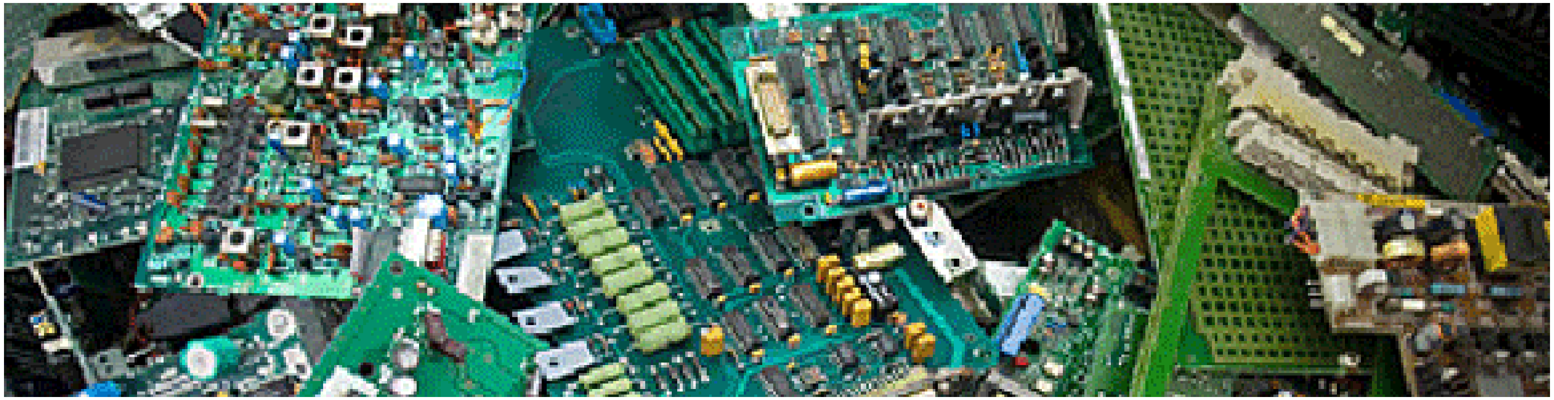


Potential biometallurgical applications

Solid waste streams: recovery of critical metals

- Phosphate fertiliser industry: by-product phosphogypsum includes lanthanum, cerium, praeseodymium and neodymium
  (Tranchida et al., *Marine Pollution Bulletin*, 2011, 62: 182-191)

- Electrical and electronic waste: bacteria and fungi can mobilise up to **95 %** of Cu, Zn, Ni, Al and Pb
  (Brandl, *Biotechnology Set*., 2008, 191-224)



Potential biometallurgical applications

Solid waste streams: process intensification

- Bioleaching is rather slow:
  releasing **1 – 6 kg metal/m^3 reactor.day**
  (Bakhtiari et al., *Inter Journal of Mineral Processing*, 2008, 86: 50-57)
- Ultrasound techniques can
  - Stimulate bacterial growth
  - Improve the process of bioleaching physically:
    - better particle erosion
    - higher availability of metals
- Intensification on a genetic level by GMO appears possible (De Corte et al.; labMET)

Potential biometallurgical applications

Solid waste streams: slag valorisation

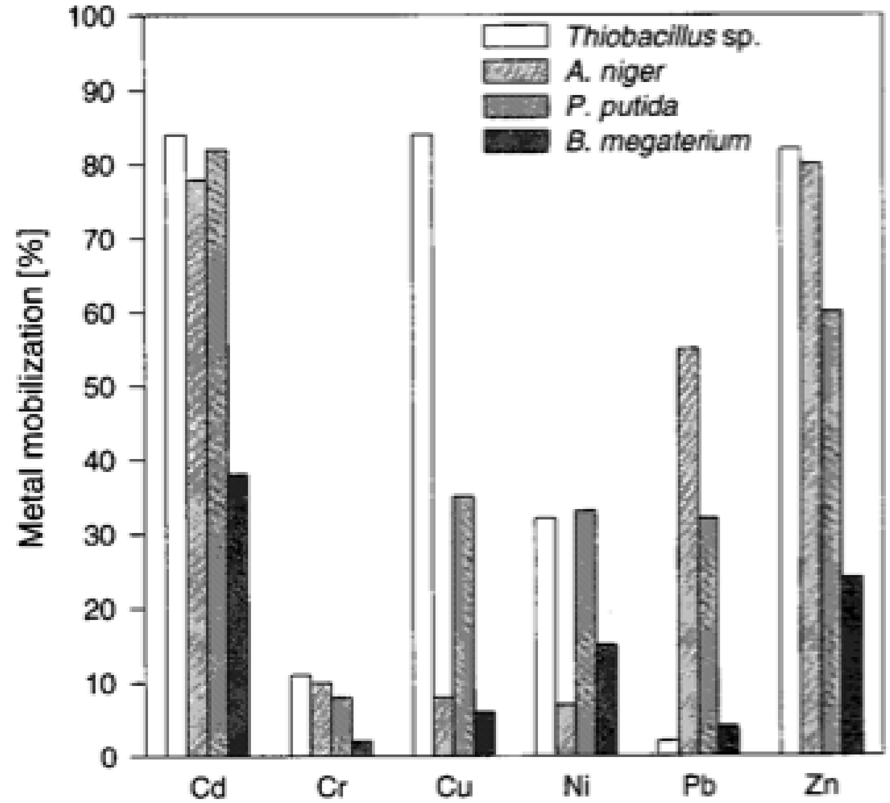
- Bottom ashes and slags of waste incineration processes:
  Al, Pb, Cr, Zn, Se, Sr, Ba and Cs in µ g – mg/g levels
  (De Boom et al., *Waste Management*, 2011, 31: 1505-1513)

- Application of biometallurgy:
  - recovery of valuable metals
  - detoxification of industrial waste for a less hazardous deposition and leaching prevention

Potential biometallurgical applications

Solid waste streams: slag valorisation by bioleaching

- Bioleaching is a low-cost and low-energy level technology compared with thermal treatment
- Leaching of fly ash from municipal waste incineration with four different micro-organisms (Brandl, *Biotechnology Set.*, 2008, 191-224)



Take home: More > **30 % mobilization** of Cd, Cu, Ni, Pb and Zn in 16 days

Potential biometallurgical applications

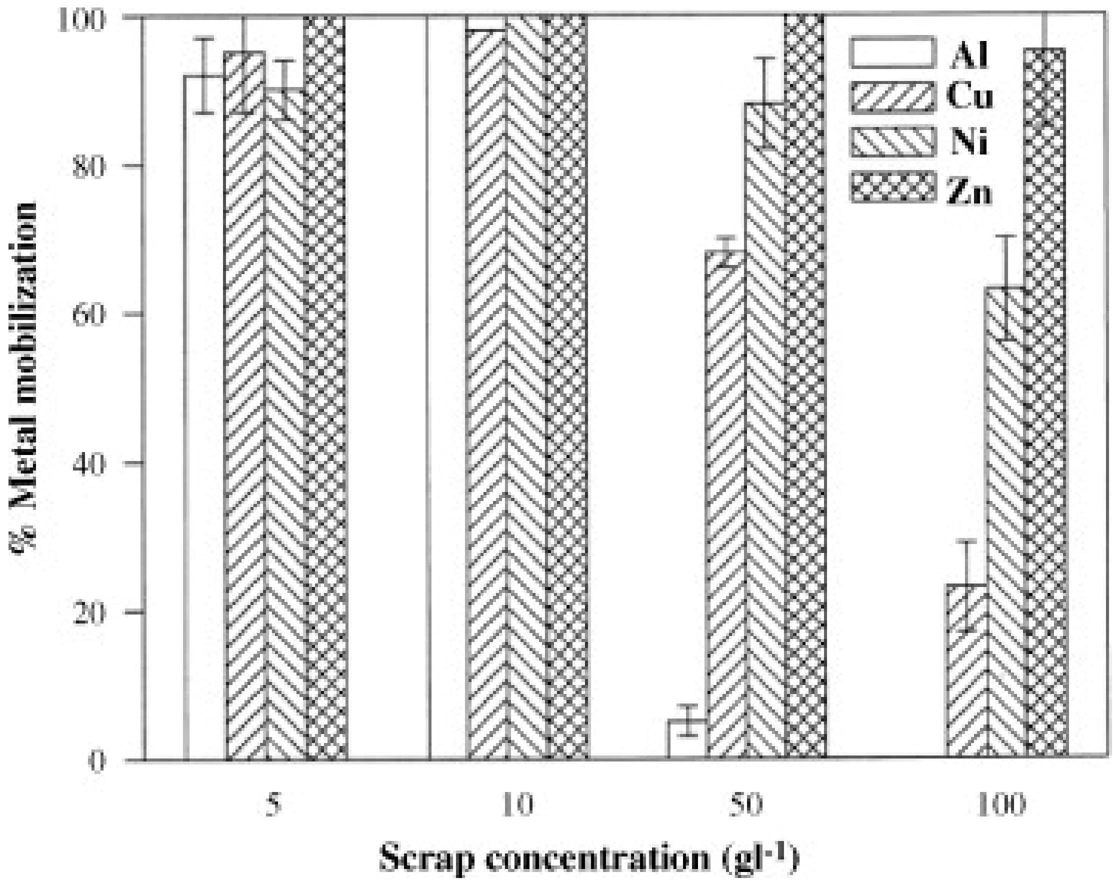
Solid waste streams: slag valorisation by bioleaching

- Slag waste of copper smelting industry:
  Leaching of **41% Fe, 62% Cu, 35% Zn and 44% Ni in 29 days**
  In second phase precipitation by sulphate-reducing bacteria: up to 98% Cu and 99% Zn
  (Kaksonen et al, *Minerals Engineering*, 2011, 4: 1113-1121)

- Pb/Zn smelting slag using thermophilic bacteria:
  Leaching of **86-91% As, 90-93% Cu, 90-94% Mn and 81-87% Zn in 6 days**
  (Guo et al., *Hydrometallurgy*, 2010, 104: 25-31)

Potential biometallurgical applications

Solid waste streams: electronic scrap valorisation



(Cui et al., *Journal of Hazardous Materials*, 2008, 158: 228-256)

Take home: More **> 90** % leaching of Al, Cu, Ni and Zn in 10 days at scrap concentrations of 5 and 10 g/L

+ Biometallurgy in Ghent University

- LabMET: S. Maes – K. Rabaey – N. Boon
  Bio-based recovery processes
- Department of Materials Science: K. Verbeken
  Analysis of biometals by advanced visualisation techniques
- Ecochem: G. Du Laing
  Metal analysis and speciation
- PAINT: P. Van der Meeren – A. Verliefde
  Particle characterization
- EnVOC: H. Van Langenhove – J. Dewulf
  Gas (bio)treatment – clean technology/LCA
- COMOC: P. Van Der Voort
  Sorption of metals from diluted waste streams
- Coordination by W. Verstraete

Conclusions

- Bacteria deal in various ways with soluble metals but also with insoluble metals

- We can engineer bacteria
  - Special strains/GMO constructs
  - Special teams/microbiomes

Conclusions

- Bacteria are used for removal and recovery of metals from
  - Liquid waste streams through biosorption /electro-deposition
  - Solid waste streams through acid production and bioleaching

- Complementary combination of biological and more conventional techniques is under development.

Adequate recovery with minimum of environmental burdens and energy input becomes achievable